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Critical Fluid Systems, Inc., Cambridge, MA

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PILOT PLANT EVALUATION OF CRITICAL FLUID EXTRACTIONS FOR ENVIRONMENTAL APPLICATIONS

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16. ABSTRACT The report gives results of using liquefied-gas solvents in a pilot plant study to extract oil from mill scale (a steel mill by-product) and bleaching clay (a vegetable oil filtering media). The process, operated on a semi-batch cycle, involved two extractors and a solvent recovery system. The results of the extraction experiments demonstrated the feasibility of condensed gas extraction. Preliminary economics indicate attractive payback on full-scale plants: about 23 months for a mill scale extraction facility and 17 months for a bleaching clay plant.

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Liquefied Gases	Oil Extraction	11K
Solvents	Critical Fluids	07A, 13I
Extractors	Bleaching Clay	11F
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ABSTRACT

Liquefied gas solvents were used in a pilot plant study to extract oil from mill scale, a steel mill by-product, and bleaching clay, a vegetable oil filtering media. The process was operated on a semi-batch cycle; the equipment consisted of two extractors and a solvent recovery system. The results of the extraction experiments demonstrated the feasibility of condensed gas extraction. Preliminary economics indicate attractive payback on full-scale plants -- approximately 23 months for a mill scale extraction facility and 17 months for a bleaching clay plant.

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I. CONCLUSIONS

1. Steel mill scales containing several percent residual oil can be de-oiled to levels acceptable for sinter-plant feed using condensed dichlorodiflouromethane (Solvent-12), at ambient temperatures and pressures of about 700 kPa. The maximum pressure requirement of such a system is 1400 kPa.

2. The rate of mill scale extraction is proportional to flow rate. Ninety percent extraction occurred in 30 minutes at 1.6 kg/min and in 60 minutes at 0.9 kg/min.

3. The rate of mill scale extraction was increased by a static soaking period before extraction.

4. Preliminary economic evaluation indicates that credits for de-oiled mill scale and fuel quality oil provide an attractive payout for a plant de-oiling 80 metric tons per year of 5% oil mill scale feed.

5. Bleaching clays used in vegetable oil processing can be de-oiled using the condensed gas extraction process.

6. Extraction efficiency of bleaching clay is primarily a function of contact time.

7. Preliminary economic analysis indicates that product recovery credits and disposal cost reduction make condensed gas extraction attractive.

II. INTRODUCTION

Near Critical and Supercritical Fluids as Solvents

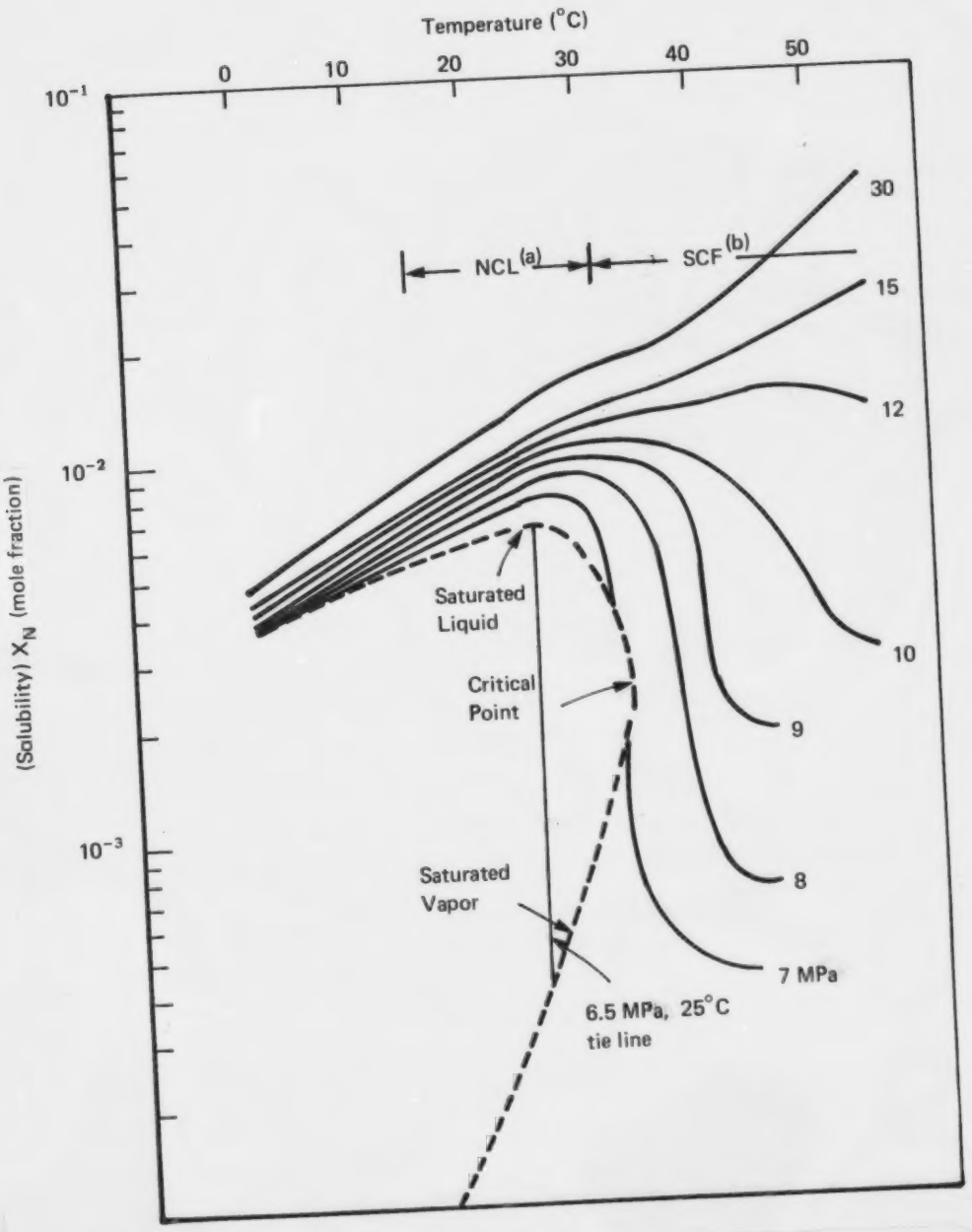
The use of near-critical and supercritical fluids as solvents for extraction has been of interest for at least 20 years. Successful applications have been developed where the economic gains offset the costs of high pressure operation. Two components of that gain are:

1. Credits for by-product recovery.
2. Reduced processing costs.

A "critical fluid" is a fluid near its thermodynamic critical temperature and pressure. At the critical point there is no distinct liquid or vapor state. The various properties of the fluid in this state (e.g., density, viscosity, diffusivity) are intermediate between the corresponding values of the fluid in the gas and liquid states. Further, these properties are not fixed. They can be varied by manipulating temperatures and/or pressures. Not only are these physical properties variable above the critical point, so also are the solubilities of organic solutes. This can be observed in Figure 1, a solubility map of naphthalene in near- and supercritical carbon dioxide. This diagram is based on published solubility data in the near-critical region(1) taken with data on the solubility of naphthalene in saturated CO_2(2). We see in this diagram fairly conventional solute behavior in the region of 0 to 25 C. Solubility increases with increasing temperature and, at a given temperature, increases with pressure. As we approach the critical temperature, however, we observe markedly different behavior. At pressures near the critical pressure (7.5 mPa) the solubility sharply decreases with increasing temperature. The effect becomes less pronounced as pressure is increased, but it is clear that near the critical pressure solubility is a strong function of temperature. Thus we see that operation in the near critical and supercritical regime allows the process designer to tailor the solvent to the particular extraction under consideration.

A number of fluids have been proposed for use as extraction solvents. Some of these fluids have been listed in Table 1 along with their critical properties.

The need for the subtleties of supercritical fluid extraction is not always present. This is true in the two cases taken up in this report. The residual oils on both steel mill wastes and bleaching clays are soluble in liquefied gas solvents such as propane and Solvent-12 well below critical conditions. This allows processing at ambient temperatures and at pressures that do not require exotic materials or methods of construction. All of the economic advantages of supercritical extractions still exist (simple solvent recovery, high purity, easily desolventized products, low operating cost) with the added benefit of lower equipment costs. In many situations, the compressor is the only energy consumer in the process requiring far less energy than conventional separation processes. This energy consideration is frequently the prime factor in making condensed gas solvent extraction, as well as near- and supercritical solvent extraction, so economically attractive.



(a) NCL = Near Critical Liquid
(b) SCF = Super Critical Fluid

FIGURE 1 SOLUBILITY OF NAPHTHALENE IN CARBON DIOXIDE NEAR ITS CRITICAL POINT

1 atm. = .1013 MPa

TABLE I

CRITICAL PROPERTIES FOR SELECTED FLUIDS

FLUID	CRITICAL TEMPERATURE (T_c, °C)	CRITICAL PRESSURE (P_c, mPa)	CRITICAL DENSITY (P_c, g/cm3)
Pentane	296.7	3.4	0.232
Butane	152.0	3.8	0.228
Solvent-12	112.0	4.1	0.558
Propane	96.9	4.3	0.220
Ethane	32.3	4.9	0.203
Ethylene	9.9	5.2	0.227
Carbon Dioxide	31.1	7.5	0.468
Sulfur Dioxide	157.6	8.0	0.525
Ammonia	132.4	11.	0.235
Water	374.3	22.	0.326

Steel Mill Scale Oily Wastes

The steel industry is a major producer of oil-containing solid wastes. A variety of waste streams exist. These are listed in Table 2. The largest volume stream is that of mill scale. Mill scale is waste iron oxides contaminated with lubricating oil. It results from surface contamination of steel stock as stock is formed into product during rolling and handling operations. Mill scale represents 1.5 to 10% of the total raw steel production of a plant. As the percentage increases, so also does the incentive to convert this waste into recyclable material. A 1978 study (3) indicated that about half of the scale generated is recycled to the blast furnaces, most by way of a sintering operation. The other half is stockpiled.

The reason only half of the mill scale is reprocessed is that the sintering operation is adversely affected by high oil content. The oil is volatilized during sintering and recondenses in the plant off-gas. Without treatment this produces a visible plume and is an obvious source of pollution. When bag houses are used, the oil condenses and impairs bag house operation.

Potential Solutions --

Several de-oiling methods have been tested. Water washing with hot alkaline solution can remove at best 90-95% of the oil on mill scale fines at low cost. The solids would then be suitable for recycling, but the oily solid disposal problem becomes an oily water disposal problem. Thermal incineration of the oily mill scale is an effective de-oiling method but the energy costs of the incineration and the subsequent off-gas treatment could quickly offset the economic advantages of recycling the iron. A direct fired kiln has been reported in commercial use (4) for this alternative.

TABLE 2

IRON-CONTAINING SOLID WASTES GENERATED IN STEEL MILLS

	Hydrocarbon Content (%)	Iron Content (%)	Water Content (%)	Contaminants	Tonnage* (TPY)
Singer Plant Scrubger Sludge	0-2	20-40	2-40	Alkalies, Zn, Pb	400-500
Mill Scale	0.01-15	60-75	2-5	---	37,500-250,000
Scarfer Scale	0.01-0.5	70-85	5-10	---	30,000-60,000
Hot Rolling Mill Sludges	5-30	60-70	21-58	---	2,000-4,000
Cold Mill Sludges	2-7	---	81-88	Zn,Sn	5,000-7,000
Centerless Grindings	---	60-85	---	---	2,500
Waste Water Treatment Sludges	2-8	0-44	40-78	P, Zn,Cr,Sn	7,000-20,000
Creek Dredge Spoil	Neg.-2	Neg.-40	30-50	SiO_2,AL_2O_3,S	Neg.-5,000

*Based on a nominal 2.5 MTPY steel plant.

Another possibility is liquid solvent washing using a chlorinated hydrocarbon solvent. The solvent would be used to strip the oil off of the mill scale fines thus making them suitable for the sintering operation. Prior to sintering, the solvent would have to be removed from the solids, and the solvent would have to be recovered from the product oil in order for the oil to be recycled. The energy costs for these operations would have to be evaluated and carefully compared to the recovered raw material value. The costs of solvent make-up must also be taken into account.

Condensed Gas Extraction —

An alternative that appears economical is based on condensed gases. The effectiveness of the conventional solvent process can be coupled with the economic attractiveness of critical fluid extraction to yield a process that holds the promise of efficient extraction at reasonable processing costs. This process uses sub-cooled, condensed gases as the solvent. After extraction, the clean scale is depressurized to atmospheric conditions. Residual solvent vaporizes within a short time leaving the de-oiled scale ready for recycling. The oil-laden solvent is sent to a still where the oil is concentrated and the solvent vaporized for reuse.

The energy for this vaporization comes from the superheated compressor discharge, which is routed through heat exchange coils located in the base (reboiler section) of the still. Thus the only energy input into the system is the compressor.

TABLE 3

MAGNITUDE OF BLEACHING CLAY WASTE

U.S. Vegetable Oil Production:	5.5×10^9 Kg Annually
Typical Clay Usage:	0.5 Kg/100 Kg Refined Oil
Waste Clay Oil Content:	30% (mass)
U.S. Waste Clay Production:	35.7×10^6 Kg Annually, or 102,000 Kg/Day (350 day/year)

Bleaching Clay Oily Residues

The refining of a number of synthetic and natural oils includes a processing step to decolorize, or bleach, the refined product using special clays. These clays are composed of very fine (<400 mesh) diatomaceous earth particles and a number of additives. The clay is mixed with the oil, from which it adsorbs impurities from the product. The suspension is then filtered. The resulting clay filter cake contains 30 to 60% (by mass) occluded oil, and thus represents a pollution problem as well as a yield loss. About 0.5 Kg of clay is used per 100 Kg refined oil product in vegetable oil processing. The magnitude of the problem is shown in Table 3.

There are a number of incentives for recovering this oil. The first of these incentives is the potential savings in hauling and landfill costs. The mass of material handled would be substantially lower, and, with the waste clay itself being de-oiled, would require a less secure landfill for its disposal. The cost per kilogram of disposal would be lower as would the total amount of waste to be disposed of.

A second incentive is the recovery of the bleached oil product. This product could be added to either refined or crude oil, depending on its quality, and thus improve overall plant yield. The de-oiled clay may also be reusable if its activity has not been entirely spent.

A final incentive to de-oil spent bleaching clays is one of safety. The stored oily clay waste can undergo spontaneous combustion. This possibility would be lessened, if not eliminated, by de-oiling the material. Currently, water is added to the clays to inhibit spontaneous combustion. This adds to the mass to be disposed and to disposal costs.

There appear to be no de-oiling schemes in current industrial usage. As with mill scale, incineration is an option, but the higher oil content may incur higher costs in off-gas clean up. Conventional halocarbon solvent extraction is a possibility, but removing the solvent from the de-oiled clays would be difficult due to the small pores present in the clays. These pores would adsorb and hold solvent by capillary condensation. The solvent-bearing clay could present a more severe pollution problem than the starting material.

Condensed gas extraction has shown promise as a de-oiling technique for bleaching clays. Laboratory scale runs produced product oil at a somewhat higher quality than the process refined oil, presumably due to the longer contact time of the occluded oil with the still-active clay. Condensed gas extraction of bleaching clays offers the same process economic advantages outlined for mill scale de-oiling, and so was chosen for further experimentation.

III. PILOT PLANT DESCRIPTION

The solids extraction plant used for this study is a unit, primarily carbon steel, mounted on a steel framework (skid) measuring 3 m by 2.5 m (10'x 8'). The primary equipment in the plant is a bank of three extractors, a reboiler/still unit, a vertical surge vessel, a compressor and compressed gas storage vessel, a pump, piping, and valves. The process flow is diagrammed in Figure 2.

The solvent first passes through a mass flow meter. The meter signal is used as an input to a computer, which in turn outputs a control signal to a control valve, thus giving flow control.

The solvent enters the extractor inlet manifold. The extractors include two 15 cm. dia x 1.5 m. long units equipped with 6 inlet and 6 outlet ports as shown in Figure 3. This configuration allows for upflow, downflow, and crossflow experimentation. The third extractor was of the same length and schedule, but had a diameter of 7.6 cm. This allowed for higher velocity experimentation in either upflow or downflow modes. This smaller column was not equipped for crossflow work.

The solvent flows through the packed solids in the extractor where it dissolves the oil from the mill scale or bleaching clay. Extractor pressure is maintained by a back pressure control loop on the column exit manifold. The pressure set on the controller ensures that the solvent passes through the extractor in a liquid phase. The solvent-oil extract flows through the pressure control valve and into a series of vapor/liquid separators. The first separator removes flashed solvent vapor from the extract and sends the vapor to the still tower at a point above the liquid inlet. The second separator is used to remove any water carried over from wet solids.

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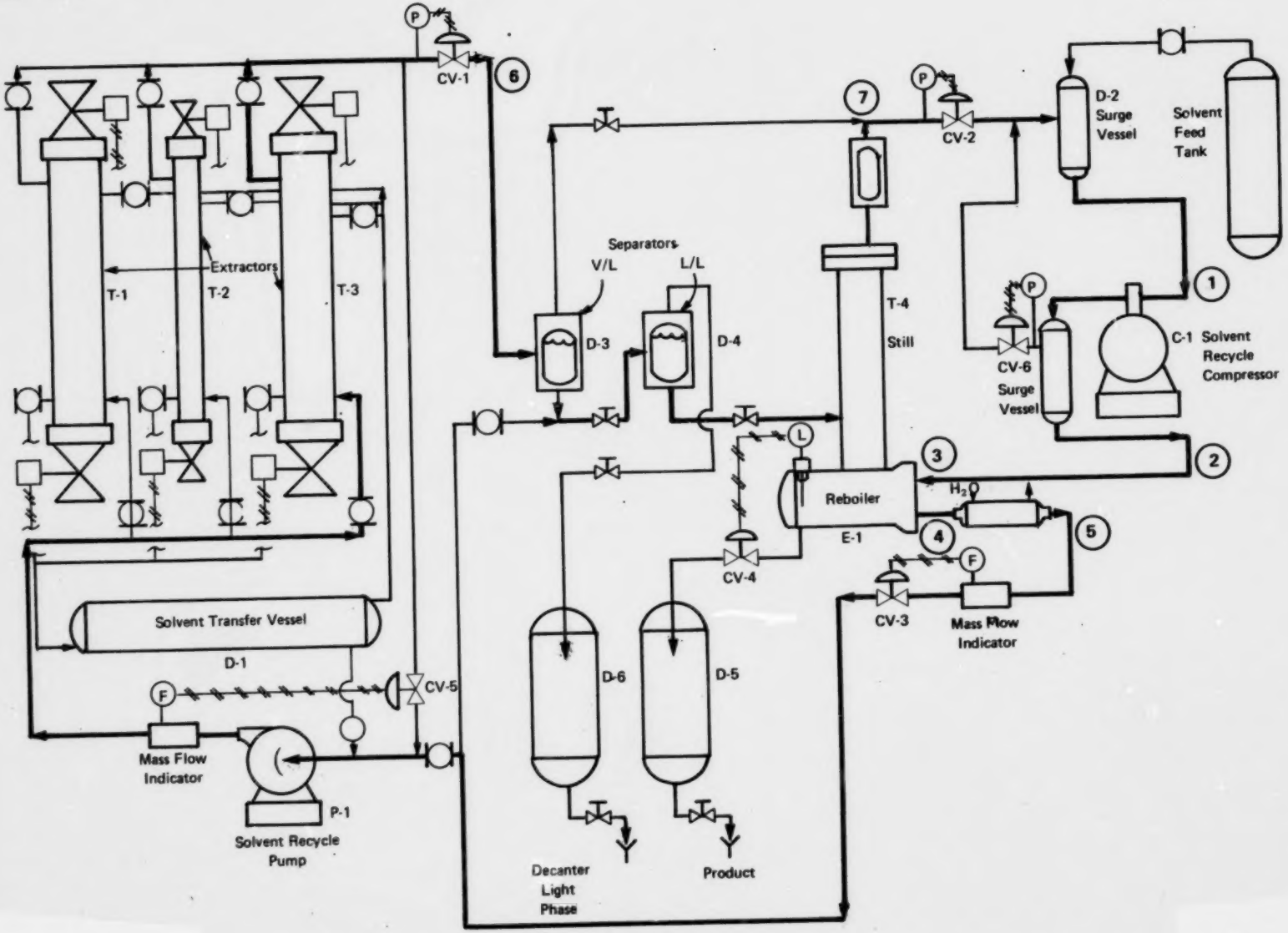

FIGURE 2 SIMPLIFIED PROCESS FLOW DIAGRAM

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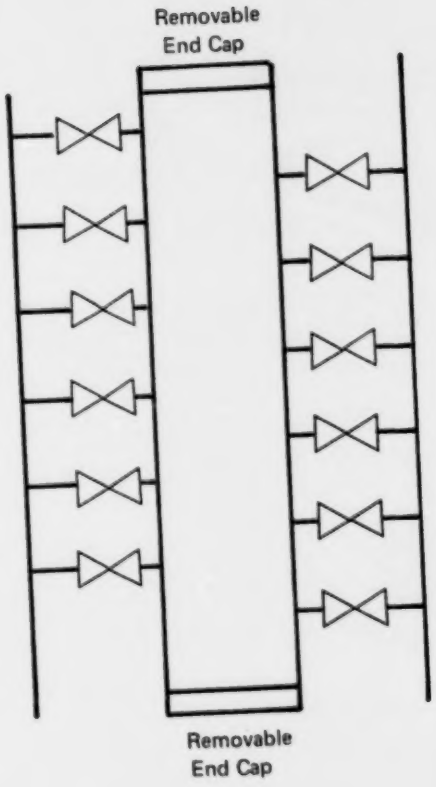


FIGURE 3 VALVE CONFIGURATION ON 15CM DIA. EXTRACTION COLUMNS

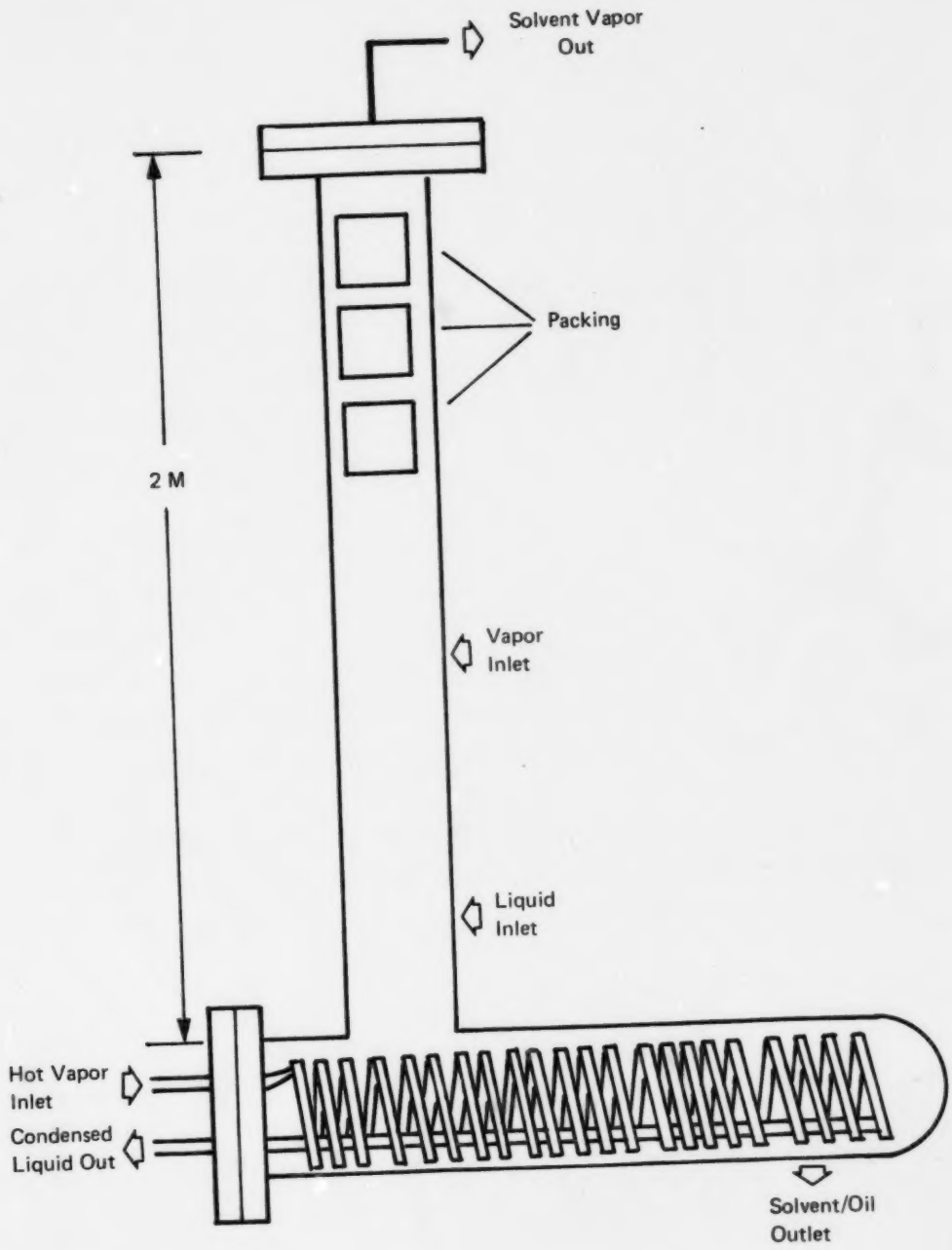


FIGURE 4 STILL/REBOILER UNIT SHOWING PACKING AND HEAT EXCHANGE COILS

The still/reboiler unit is diagrammed in Figure 4. It is a stainless steel unit capable of operating at pressures in excess of 10 mPa. (This work was carried out at pressures at less than 700 kPa.) It is a 10 cm diameter tower 2.5 m high coupled at its base to a kettle-type reboiler containing 13 meters of 1.3 cm diameter heat transfer coils. These coils allow efficient heat transfer from the superheated compressor discharge to the contents of the reboiler. It is in this reboiler that solvent is boiled off and the extracted oil concentrated. As oil builds up in the reboiler, a level control valve opens to allow an oil/solvent mixture to flash into the product receiver. In our pilot plant system, this solvent is vented to the atmosphere. The still pressure is maintained at a pressure about 250 kPa less than the extractor pressure by another (independent) back pressure control valve. The solvent vapors from the reboiler (and vapor/liquid separators) flow through this valve and into the vertical compressor inlet surge vessel.

The compressor inlet surge vessel is another 15 cm diameter steel vessel 1.5 meters high. This acts as a trap to prevent liquid carryover (if any) from the still from reaching the compressor. It also acts to dampen out the pulsations of the compressor, thus isolating the still from pressure variations. The solvent vapors pass through a Balston CX filter before entering the compressor.

The compressor is a Corken model 91 oil-less piston compressor capable of delivering 85 LPM (free air flow) and having a maximum discharge pressure of 1700 kPa. The output of the compressor is sent to a 110 l surge vessel. The pressure in this surge vessel is maintained at 1400 kPa by another back pressure control valve that vents excess compressor capacity to the compressor inlet surge vessel.

The superheated compressed solvent gas flows into the coils of the reboiler and is there liquefied as it gives up its latent heat to the solvent/oil mixture in the reboiler. The coils are followed by another vapor/liquid separator. This separator serves to collect non-condensible gases and ensure that only liquid solvent flows to the flow meter, and so through the system for another extraction cycle.

IV. EXPERIMENTAL PROCEDURES

Overview

The goal of these experiments was to collect data in three basic areas:

1. Mass Balance
2. Extraction Rate
3. Extraction Efficiency

By varying flowrates, times, and flow direction and comparing the above data for each case, we were able to optimize the extraction process for each solid.

The first step in the extraction experiment was to load the extractor with a known amount of feed. This was accomplished by weighing starting material in a transfer vessel and pouring the material into the extractor. A large funnel kept transfer losses to a minimum. Samples of the feed were taken at this time. When the transfer was complete, the transfer vessel was reweighed. The charge to the extractor was then calculated and noted, as was the height of feed in the extractor.

The extraction plant would then be started up in a bypass mode. No solvent was put through the bed of solids during this start-up phase. The flow of solvent was cycled through the piping until pressures and flow rates had achieved steady state. Not until this steady running condition was achieved would extraction begin.

The extraction cycle was begun by filling the column with solvent. This was done by the pump from the solvent storage vessel or, if the solvent volume in that vessel was inadequate,

from the main solvent supply tank. Filling the column generally took about five minutes. Pumping was continued until the pressure in the column was higher than the vapor pressure corresponding to ambient temperature, typically greater than 500 kPa. A valve at the top of the column was then slightly cracked to relieve any trapped air. The column was ready for extraction.

The inlet and outlet valve arrangement for the given experiment was set and the bypass valve switched to extraction. The solvent mass flow totalizer was re-zeroed at this time. The experiment continued for the prescribed time, and then flow was once again diverted to the bypass mode. The total solvent throughput was noted, and the extractor drained of solvent.

Draining the solvent was a two-step process. The first step entailed pressurizing the top of the column with either compressed solvent gas or with nitrogen in order to push the liquid solvent to the transfer vessel. Fine materials such as bleaching clays would clog the filters thus preventing liquid from draining. This first step was successful only with mill scale.

The second step was to flash the solvent contents of the extractor through all of the inlet and/or exit ports and into the compressor inlet. Flow from the compressor was then liquefied and sent to the solvent storage tank. When the compressor inlet showed a pressure of less than 10 psi, the flashing was discontinued and the column allowed to sit for 10 minutes. If the pressure remained low, the remaining solvent vapors were vented to the atmosphere. The extractor was next drained of solids.

Removal of solids was straightforward. After a final check to show that there was no pressure in the extractor, the top cover was opened. The height of residue was noted and the top of the bed of solids examined visually for evidence of channeling or agglomeration. A sample of the top of the bed was taken.

The bottom cover was next removed and the solids collected in a weighed container. This procedure required care in the case of bleaching clay because this material rarely poured out of its own accord. The solids would be prodded from the bottom with a rod to break up any bridging, and then prodded from the top to start the flow. Any solids escaping the collection vessel were swept up and added to the residue. The column sides were examined for adherring residue and cleaned (scraped) when necessary. Samples of the bulk residue were taken by a cone and quartering technique in an effort to get a representative sample for moisture and oil analysis.

In addition to the mass balance around the solids charged to the reactor, data allowing calculation of the amount of oil extracted was also taken. This data involved taking a sample of the reboiler contents and flashing off the solvent through a dry test meter. By collecting and weighing the residue after solvent removal, a concentration of oil in solvent in the reboiler was obtained. A level measurement was made and converted to a volume. Multiplication of these two values gave the mass of oil in the still/reboiler unit. This data was taken before and after every run, as was the weight of the product receiving vessel. Calculated values of oil collected are compared to calculated values of oil extracted giving a second mass balance around the oil.

Extraction rate data was taken by means of grab sampling the extract stream at various times during the extraction cycle. The sample's solvent was vented and the concentration of oil in the extract was calculated. When this data (Table 4) was plotted against time, an exponential decay in concentration with time was observed (Figure 5). Replotting this data using semi-log coordinates gave a slope to the decay that could be compared from run to run (Figure 6, 12, and 17). A steeper slope indicates a faster extraction.

Extraction efficiency data was based on Soxhlet extraction of feeds and residues. A composite sample of feed was taken as the column was loaded; a similar sample of residue was taken at the conclusion of the run. These samples were then analyzed for their oil content. We defined extraction efficiency as the quantity of oil removed divided by the quantity of oil available for extraction as determined by the Soxhlet analyses.

TABLE 4

EXAMPLE OF SAMPLE BOMB MASS MEASUREMENTS
USED TO DETERMINE EXTRACT OIL CONCENTRATION

#	Time (min)	Solvent Through-put (kg)	Bomb Weight (g)	Total Weight (Bomb, Solvent, and Oil) (g)	Weight of Bomb + Oil (After Venting Solvent) (g)	% oil $\frac{((6)-(4))}{((5)-(4))} \times 100$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	8	7.1	410.04	443.02	411.26	3.70
2	11	9.8	414.65	453.04	415.71	2.76
3	18	16.0	413.62	452.74	414.36	1.89
4	26	23.2	411.99	456.54	412.42	0.97

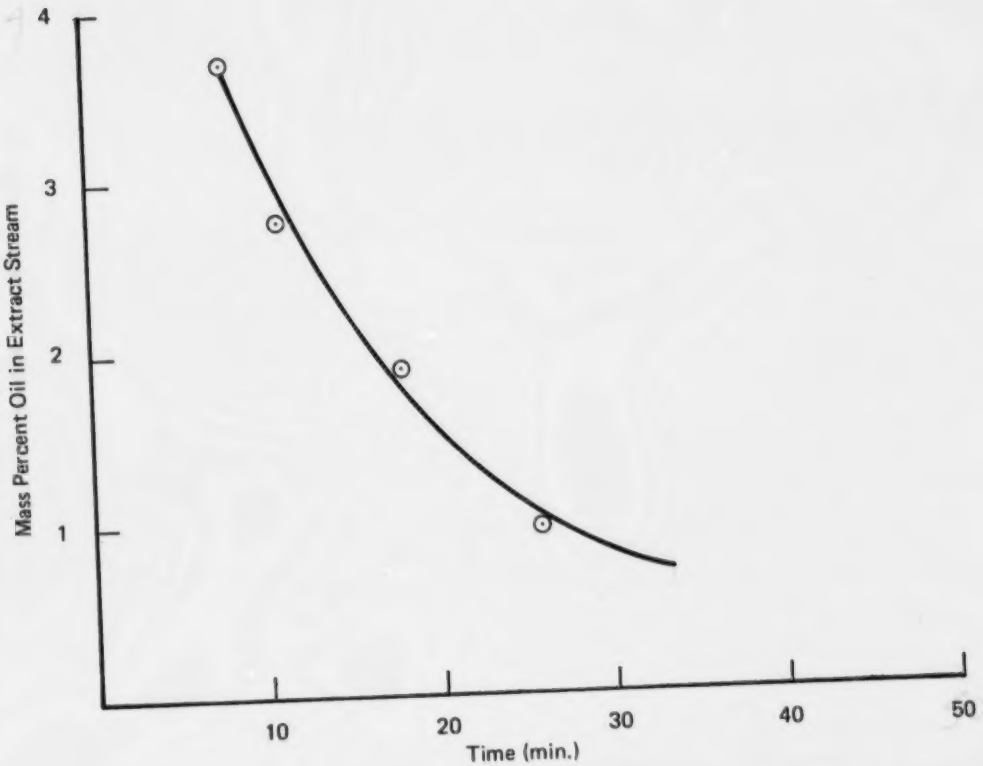


FIGURE 5 EXTRACT OIL CONCENTRATION AS A FUNCTION OF TIME DURING MILL SCALE EXTRACTION (Data of Table 4)

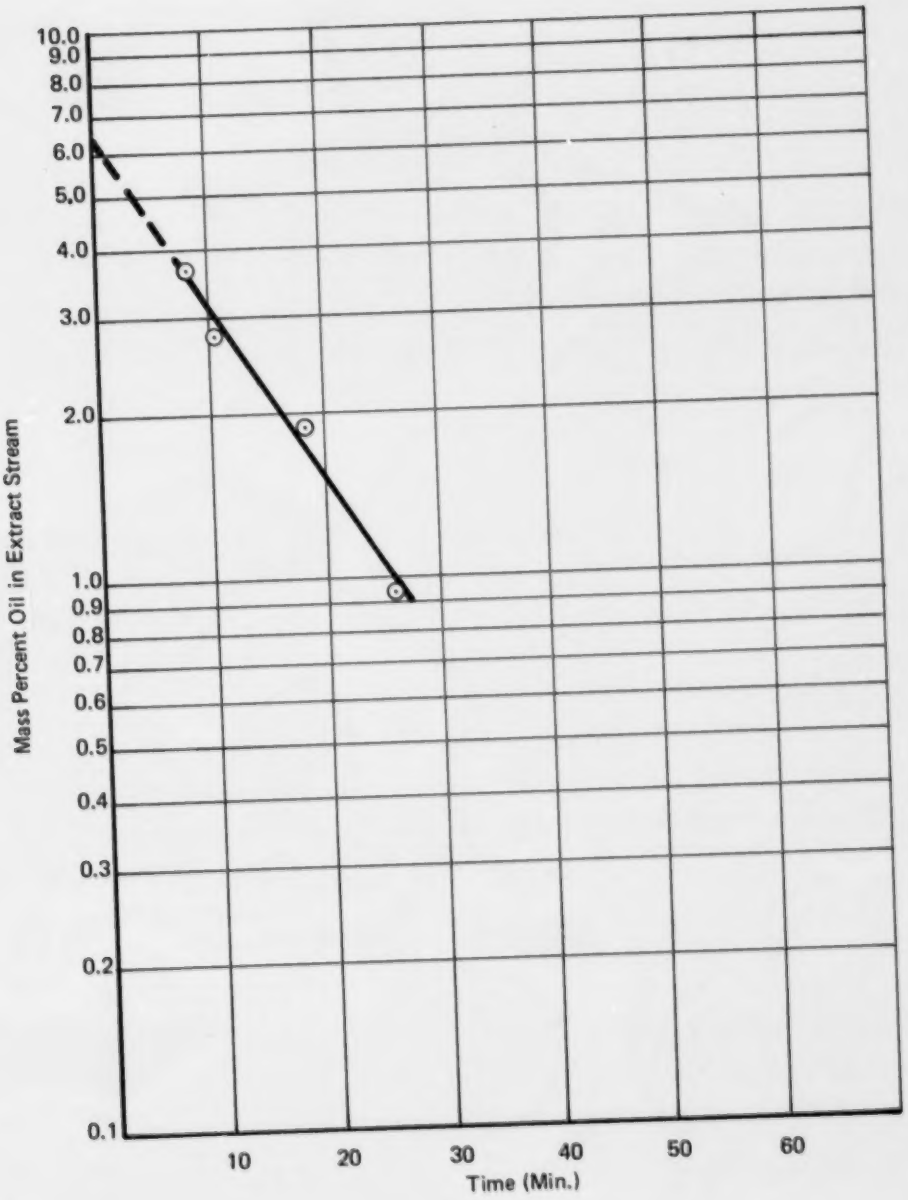


FIGURE 6 **SEMI-LOG GRAPH OF EXTRACT OIL CONCENTRATION AS A FUNCTION OF TIME DURING MILL SCALE EXTRACTION**
(Data of Table 4, see also Figure 5)

Pilot Plant Generated Data

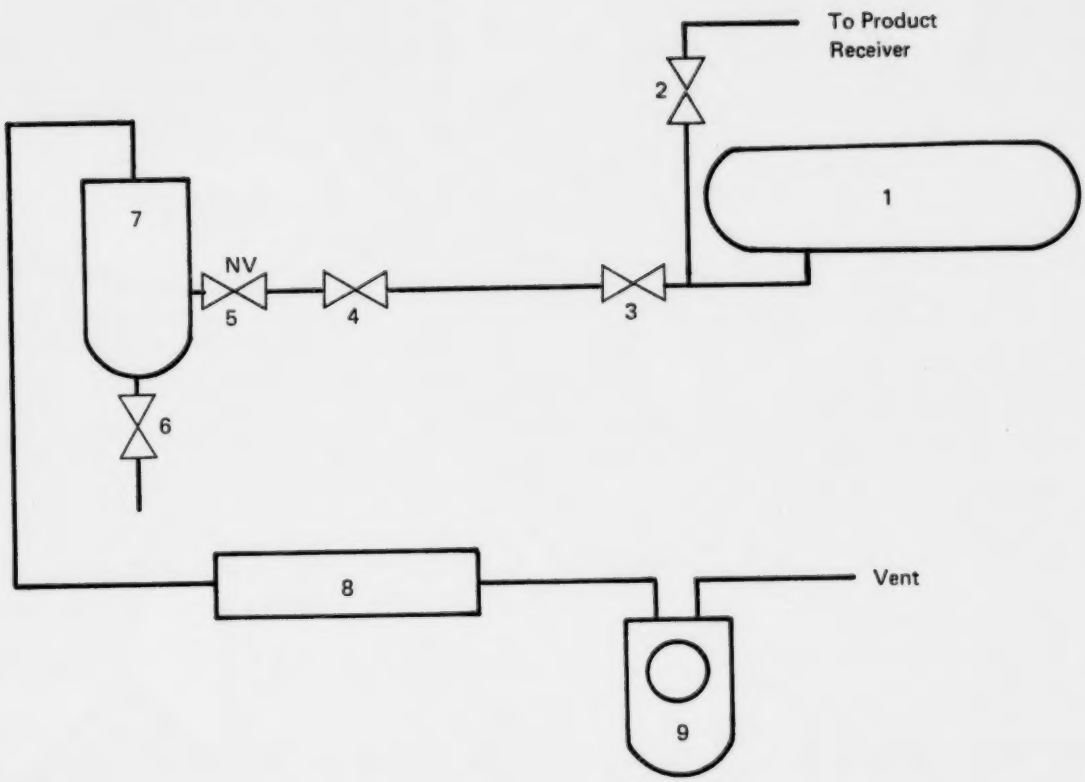
Mass Balances -- The primary tool for mass balance measurements was a Fairbanks Morse platform counterbeam scale Model 5963 with one ounce readability. This balance was used for determining the mass feed to the extractor, the mass of the residue, and the mass of oil collected in the product receiver. All weights were determined by difference. Feed was added to a weighed pail, reweighed, and added to the extractor. If the extractor would not accept the full charge, the residual was reweighed and the amount of feed was calculated. Similarly, the residue was emptied into a tared container and weighed. Any residue that escaped collection in the receiver was swept up and added to the residue bulk before the final residue mass was determined. This procedure was only necessary with the bleaching clay due to the very fine and dusty nature of the residue.

TABLE 5

TYPICAL COMPOSITIONS OF MILL SCALE AND BLEACHING CLAY FEED MATERIALS

	Mill Scale	Bleaching Clay
Moisture	4%	3%
Oil Content	1.5%	20%

The mass of product oil recovered varied between mill scale and bleaching clay due to the variations in starting material oil contents. Typical values are presented in Table 5. During mill scale runs, product oil was allowed to build up in the reboiler; the product receiver vessel was not used. Thus the value for total oil extracted in mill scale runs is a sole result of the subtraction of reboiler oil content values (before from after) as determined below. The apparatus for this determination is diagrammed in Figure 7.



1. Reboiler
2. Product Receiver Valve
3. Sampling Valve
4. Sampling Valve
5. Needle (Flash) Valve
6. Sample Drain Valve
7. Sample Flash Vessel (electrically heated)
8. Activated Carbon Dryer
9. Dry Test Meter

FIGURE 7 REBOILER SAMPLING APPARATUS

First, the flash vessel (7) would be preheated and valve 3 would be opened. The reading on the dry test meter (9) would be noted, valve 4 opened for 5 to 10 seconds, and then closed. This operation purged the 1/4" tubing line leading to the sampler. The volume of this line was calculated to be 90 cubic centimeters which, when flashed to vapor, corresponded to 23.3 liters of dry gas. The purge volume would be noted on the dry test meter when no increase in reading was observed for one minute. Purging would be repeated if 35 liters had not passed through the test meter.

When the required purge was complete, the flash vessel was drained of oil at valve six. The hot oil would drain quickly, but the vessel would be allowed to remain open for 5 minutes to ensure complete draining. Valve six would then be closed. At this time the level of liquid in the reboiler would be measured to the nearest millimeter on an attached sight glass. The dry test meter reading would again be noted, as would be the meter temperature. Valve four would again be opened for ten seconds, then closed. When the dry test meter showed no further increase in reading, the volume of gas through the meter was calculated and converted to a mass of gaseous solvent. The oil collected in the flash vessel was then drained into a tared jar and weighed on an OHAUS Dial-O-Gram Balance (Model 1650). Thus, a mass concentration of oil in the reboiler could be calculated.

The final step in the calculation used the reboiler liquid level measurement taken earlier to calculate the volume of the reboiler contents. The calculation had two regimes: the full to three-quarters empty regime and the less than one quarter full regime.

The first regime utilized data obtained directly from a calibration curve of the reboiler sight glass scale (Figure 8). This curve was generated by pouring water into the vessel in 0.5 liter increments and noting the liquid level in the sight glass. 4 liters of water were required before the first reading due to a break in the visible range of the sight glass (Figure 9). This break necessitated the use of a calculation scheme for the second regime. A linear interpolation of volume was used when the reboiler level was in this regime.

The second regime required an estimation of the reboiler liquid height. The level of liquid was visible in the sight glass, but a precise reading across the meniscus was not possible (Figure 9).

An estimate would be made based on the length of wall visible between the liquid surface and the bottom of the window. This estimate would be used in the calculation scheme to determine the liquid level in the reboiler. The results of this calculation are plotted on Figure 8 for comparison to the curve determined by direct calibration.

The above determined data allowed a calculation of the oil volume at the reboil extractor/still unit. Multiplication of the volume of liquid in the still/reboiler by the mass concentration yields a value for the mass of oil in this unit. As this sampling occurred before and after each run, a mass of oil gained (or lost) in the reboiler/still during the run was determined.

During bleaching clay experiments, the product receiver vessel was used. This vessel was disconnected from the system and weighed before and after a run. The mass increase of the product receiver was added to the mass of oil gained in the reboiler. This total is reported as total oil extracted.

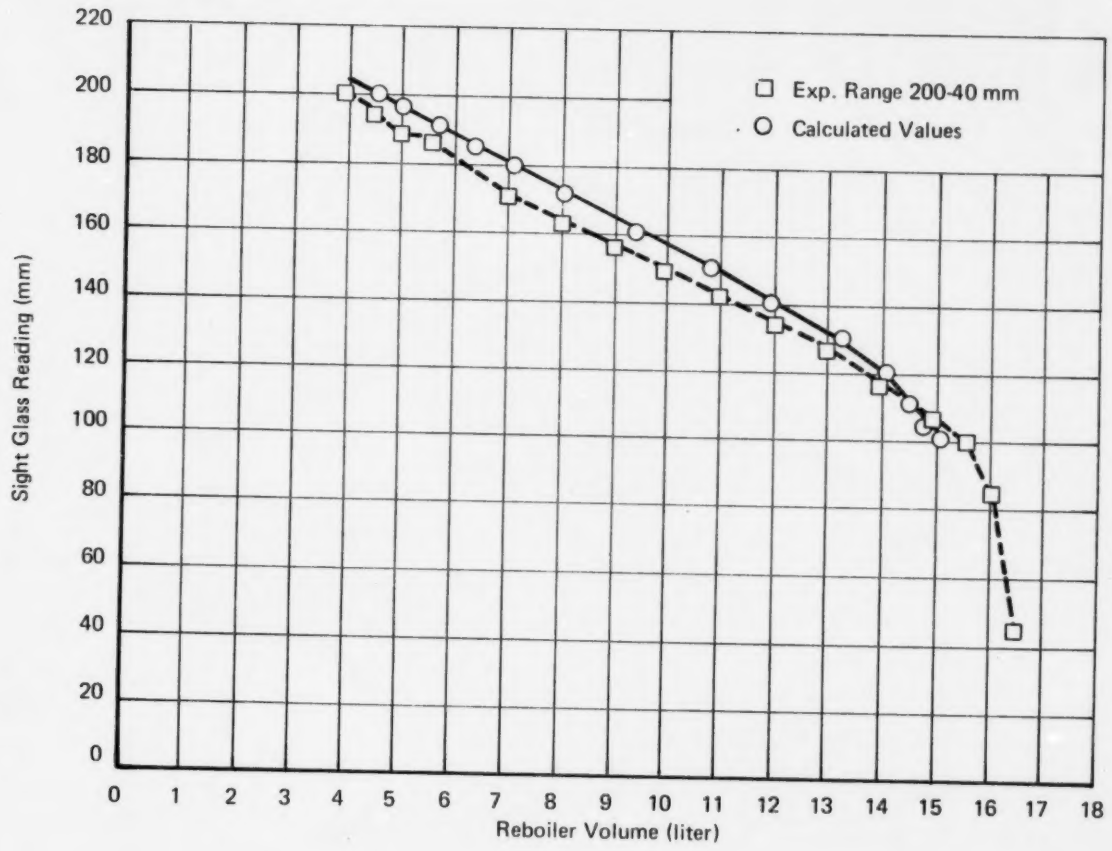


FIGURE 8 GRAPH FOR DETERMINING REBOILER VOLUME FROM SIGHT GLASS READING INCLUDING CURVE GENERATED BY CALCULATION

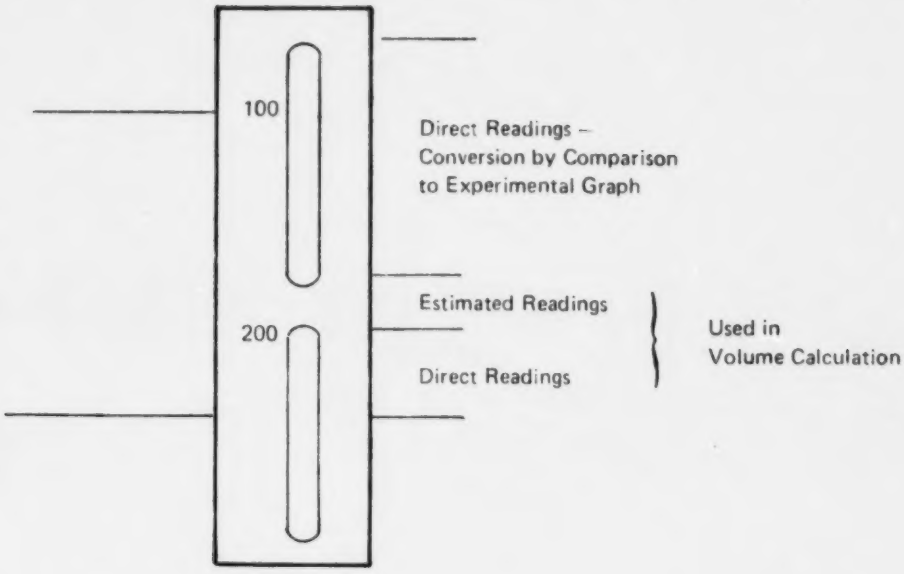


FIGURE 9 SIGHT GLASS FOR DETERMINING REBOILER VOLUME

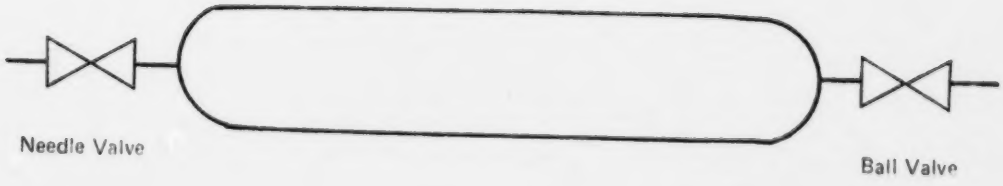


FIGURE 10 SAMPLING BOMB FOR RATE DATA

Rate Data - Extraction rate data was determined during a run by taking grab samples of the extract stream and determining the concentration of oil in the solvent. A sample bomb for this purpose is shown in Figure 10.

The clean bomb was pre-weighed on a top-loading Mettler balance and the opened needle valve end attached to the sampling point. The bomb was pressurized by opening the sample point valve. At a predetermined time, the ball valve end (open to the atmosphere) was opened for three seconds. The needle valve and the sample point valve were then closed and the sampler removed and reweighed.

After weighing, the sampler was held on end and the upper (needle) valve slightly opened. This allowed controlled venting of solvent liquid as it flashed into vapor, thus concentrating any oil at the bottom of the sampler. After venting (about one hour) the sampler was placed in a 100 C oven for 15 minutes to drive off residual solvent. The sampler was then reweighed and a mass concentration of oil in the solvent calculated. Typical values for these weights and times appear in Table 4; the curves from these data appear in Figures 5 and 6.

Laboratory Generated Data

Feed and Residue Analyses - Feed and residue analyses were performed in Critical Fluid Systems' analytical laboratory. The analyses performed were moisture and oil determinations. A Mettler analytical balance provided all mass measurements.

Moisture is defined for our purposes as weight lost after overnight drying at 100 C. Highly volatile organics were not expected in our samples. They are not present in the lubricants used in the steel mills. They are not expected in the bleaching clays due to the high operating temperature of bleaching clay filter presses (>150 C).

A sample of material would be weighed onto a drying disc, baked overnight, and reweighed. Percent moisture was then calculated and the dried residue used for soxhlet extraction.

Solvent for Soxhlet extraction varied for the two test materials. For mill scale Freon-113 was used. An extraction time of four hours proved sufficient for complete oil removal. Bleaching clays required a longer extraction period and chloroform as solvent. Thirty-six hours were required for bleaching clay analysis.

Material for Soxhlet analysis was placed in a tared Whatman extraction thimble and weighed. The thimble was then placed in an extraction apparatus, the flask of which was of known weight. The extraction would then begin and was checked periodically to ensure continued operation. After the requisite time, the thimble/sample was dried in a 100 C oven for 2 hours and the solvent evaporated under reduced pressure in a vacuum oven overnight. Weights were then taken and mass extracted was calculated based on both solids remaining and oil recovered. In determining plant extraction efficiency, the oil content based on oil recovered (mass change of flask) was used.

V. RESULTS

Mill Scale

Table 6 presents the feed and residue analyses, along with pertinent run data, for six mill scale extractions. With one exception, all residues had a residual oil level less than 0.2 mass percent. Soxhlet analyses at the low oil levels encountered in both feed and residue samples are subject to a variety of potential inaccuracies. (See Appendix A, Quality Control Evaluation Report.) In addition to potential inaccuracies in analyses, the feed and residue were not homogeneous. All efforts were taken to take representative samples (see Appendix A), but statistical uncertainty as to the representitive nature of the sample still existed. The residual oil analysis of run 30 appeared high, especially in the light of the high solvent-to-feed ratio used in that run. This could have been due to an analytical or sampling error, and resulted in a low value for oil reduction effiency for this run. It is clear that an extraction level of 75% or greater was routinely achieved.

Figure 11 shows a chromatographic effect observed in a partial mill scale extraction. This figure shows residue analyses at various levels in the three inch column after a thirty-minute downflow extraction. These samples were taken by opening ports in the extractor and withdrawing a sample from the immediate vicinity of the port. Top and bottom samples were taken from the feed and exhaust ports, respectively. Some interesting points can be noted.

TABLE 6

MILL SCALE FEED AND RESIDUE ANALYSIS,
RUN CONDITIONS, AND OIL REMOVAL EFFICIENCIES

RUN	30	31	32	35	36	37
FEED OIL (Mass %)	1.2	1.2	0.9	2.4	1.2	1.0
Moisture (Mass %)	1.1	3.4	3.9	3.4	2.5	3.5
RESIDUE OIL (Mass %)	0.4	0.1	0.2	0.1	0.1	0.2
Moisture (Mass %)	0.6	1.3	1.0	0.1	0.4	0.7
SOLVENT MASS FLOWRATE (Kg/Min)	0.9	1.6	1.1	1.0	1.4	0.5
SOLVENT-TO-FEED RATIO	4.0	4.0	1.0	2.5	2.6	1.3
TIME FOR EXTRACTION	160	94	30[a]	89	62	83
DIRECTION	Upflow	Upflow	Upflow	Down	Down	Down
OIL REDUCTION EFFICIENCY[b] (%)	67	92	78	96	92	80

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[a] A thirty-minute soak period preceded extraction

[b] $\text{Efficiency} = \frac{\text{Feed Oil (\%)} - \text{Residual Oil (\%)}}{\text{Feed Oil (\%)}} \times 100\%$

TABLE 7

MILL SCALE MASS BALANCES

RUN	30	31	32	35	36	37
MASS CHARGED[1] kg	35.9	36.3	34.3	36.5	35.0	33.6
SOLIDS[2] Kg	35.1	34.7	32.5	34.3	33.8	33.1
OIL[2] Kg	0.4	0.4	0.3	0.9	0.4	0.3
MOISTURE[2] Kg	0.4	1.2	1.3	1.3	0.9	1.2
RESIDUE RECOVERED Kg	34.6	34.2	31.6	33.9	33.9	32.4
SOLIDS[2] Kg	34.5	33.8	31.2	33.8	33.8	32.1
OIL[2] Kg	0.1	0.03	0.6	0.03	0.03	0.06
MOISTURE[2] Kg	0.0	0.4	0.3	0.04	0.1	0.2
SOLIDS RECOVERY[3]	0.98	0.97	0.96	0.99	1.00	0.97
EXTRACTION EFFICIENCY [2,4]	75.0%	92.5%	80.0%	96.7%	92.5%	80.0%
TOTAL OIL COLLECTED [5] kg	0.39	0.01	0.82	0.15	0.93	0.86
OIL RECOVERY RATIO[6]	1.3	0.03	3.4	0.17	2.5	3.6

[1] As Received

[2] Based on Soxhlet Analysis of feed and residue.

[3] Dry residue recovered - dry solids charged.

[4] [(Oil in Feed - Oil in Residue) ÷ Oil in Feed] x 100

[5] Calculated amount based on reboiler oil content

[6] Total Oil Collected÷ (Oil in Feed - Oil in Residue)

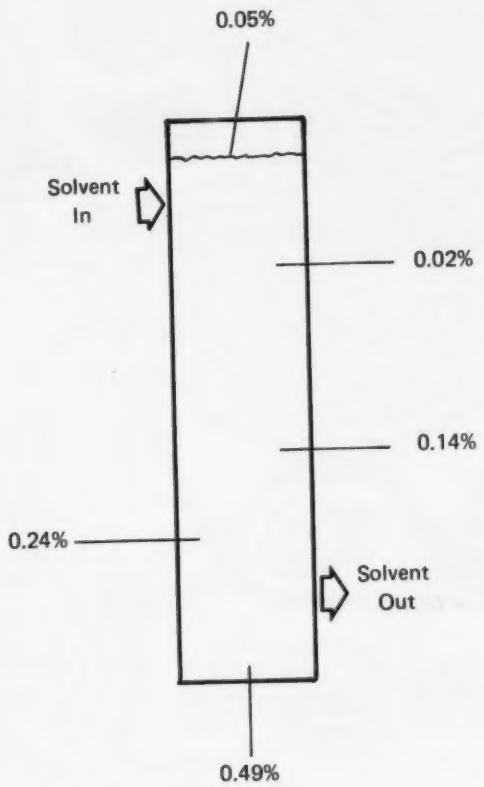

FIGURE 11 DISTRIBUTION OF RESIDUAL OIL ON MILL SCALE AFTER A 30-MINUTE DOWNFLOW EXTRACTION (Feed Oil Content 0.15%)

The sample at the top has a higher oil content than that of the first port down. This is due to the solids level in the extractor being above the solvent feed point. Solvent flow in this upper region was by diffusion only, yet extraction still occurred, probably because of the enhanced diffusivity of condensed gases.

The oil level values increased progressing down the column. This was not surprising in light of the flow direction. What was surprising was that the values are higher than the feed for the bottom two sampling points. This was a result of two effects. The first of these applied to the bottom sample. It was out of the flow pattern as in the case of the top sample of solvent since it was below the exit port. The distance in this case was, however, greater. The second effect, which applied to both lower samples (and to the rest of the samples to a lesser degree) was a result of our draining procedure. We found it difficult to drain liquid solvent out of a bed after a run due to a combination of insufficient filter area and filter plugging. Occasionally this led to flashing of the solvent to depressurize the extraction column. In an incomplete extraction, the solvent dissolved an amount of oil that was redeposited on the mill scale as solvent evaporated. Thus, oil was concentrated at the bottom of the column. This effect probably occurred in all runs, the degree of concentration lessening for more complete extractions. Sampling of residues required a cone-and-quartering technique to minimize oil content variability with position in the column.

The values of Soxhlet analyses on feeds and residues were used in conjunction with feed and residue masses to generate Table 7, a summation of mass balances for six mill scale runs. In addition to Soxhlet generated data, the oil collected per run is presented, and a recovery calculated based on the oil

collected in the reboiler divided by the oil lost as determined by Soxhlet analysis of the feed and residue samples. Also calculated was a solids recovery comparing dry, oil-free solid residue to dry, oil-free solid feed. This value is seen to be greater than 0.95 for all runs.

A problem was noted in the oil recovery values. These widely varying values were the result of difficulties in measuring small oil gains in a fairly large system (see Appendix A). Also, a possible explaination was the presence of a decanter located in the process before the reboiler, where oil gain was measured. This decanter had a significant volume (six liter) and may have held up oil. An effort was made to run the system in a by-pass mode (no extraction columns) in order to transfer the decanter contents into the reboiler after a run, but our success was limited. Incomplete system de-oiling before the runs was another suspected cause of the high value. Finally, an erroneous Soxhlet value of, for example, the feed of run 35 could also have accounted for some of the discrepancy.

Rate data on the upflow runs (30-32) was obtained by grab sampling the extract stream after the extractor. The oil concentration is plotted against time in Figure 12 and as a function of solvent-to-feed ratio (on a mass basis) in Figure 13. The concentrations in Figures 12 and 13 together with the flow rates have been used to calculate the cumulative oil extracted which is plotted in Figures 14 and 15 as a function of time and solvent-to-feed ratio.

The concentration of oil in the extract stream decreased continuously as each extraction experiment progressed as shown in Figures 12 and 13. In general, a decrease in the flow rate gave a decrease in the rate at which the concentration of oil dropped

off (see Figure 12). The large shift of the curve when the flow rate was 1.1 Kg/min is due to the 30 minute soaking period during which no extract was taken off.

The extracted oil concentration as a function of the solvent-to-feed ratio graph (Figure 13) showed that the extracted oil is recovered with lower solvent usage when the mill scale is soaked in solvent prior to extraction.

In Figure 14, the total oil extracted is plotted against time. This is the calculated area under the curve in Figure 12. The mill scale was de-oiled in the shortest time period when the highest solvent flow rate is used, with 90% oil extraction achieved in 30 minutes and 95% in 50 minutes.

Figure 15, based on the same data as Figure 13, shows that the soaking allowed the greatest degree of extraction for a given solvent usage. The first few points of the "no soak" extractions are virtually identical. However, as the extraction approached completion, higher solvent velocities continued to extract oil while more residual oil was left on the mill scale exposed to the lower velocities.

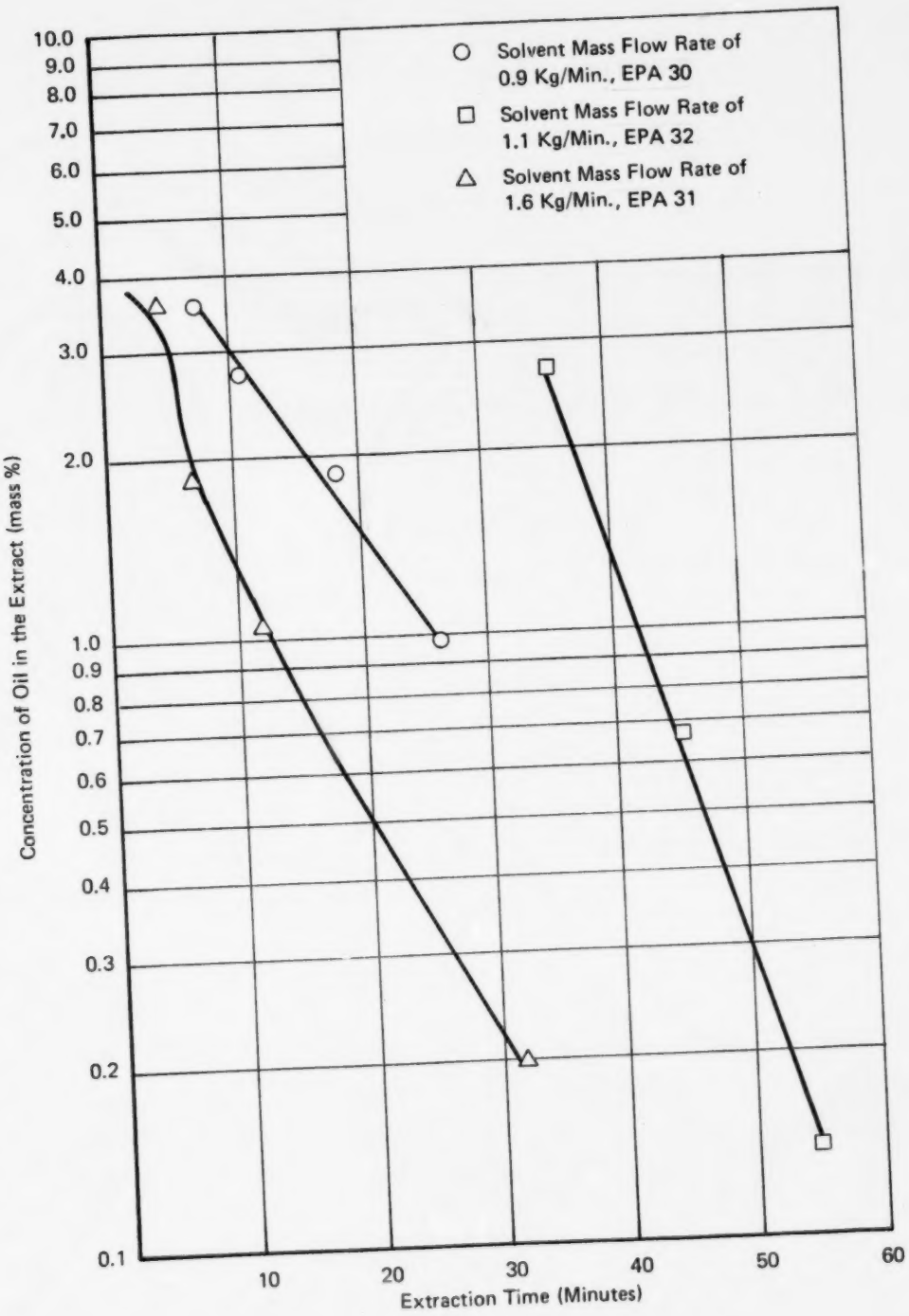

FIGURE 12 OIL CONCENTRATION IN MILL SCALE EXTRACT AS A FUNCTION OF TIME

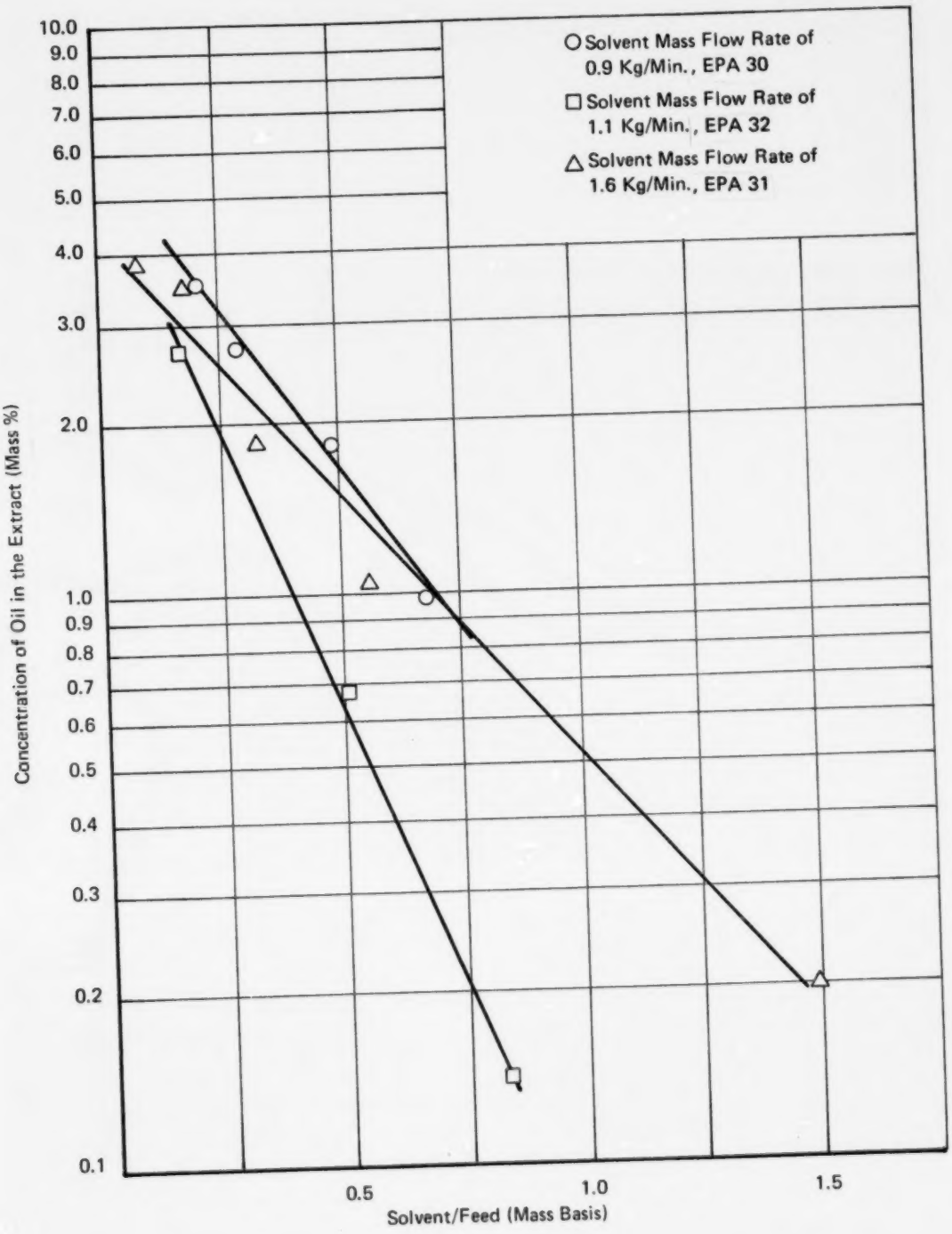

FIGURE 13 OIL CONCENTRATION IN MILL SCALE EXTRACT AS A FUNCTION OF SOLVENT-TO-FEED RATIO

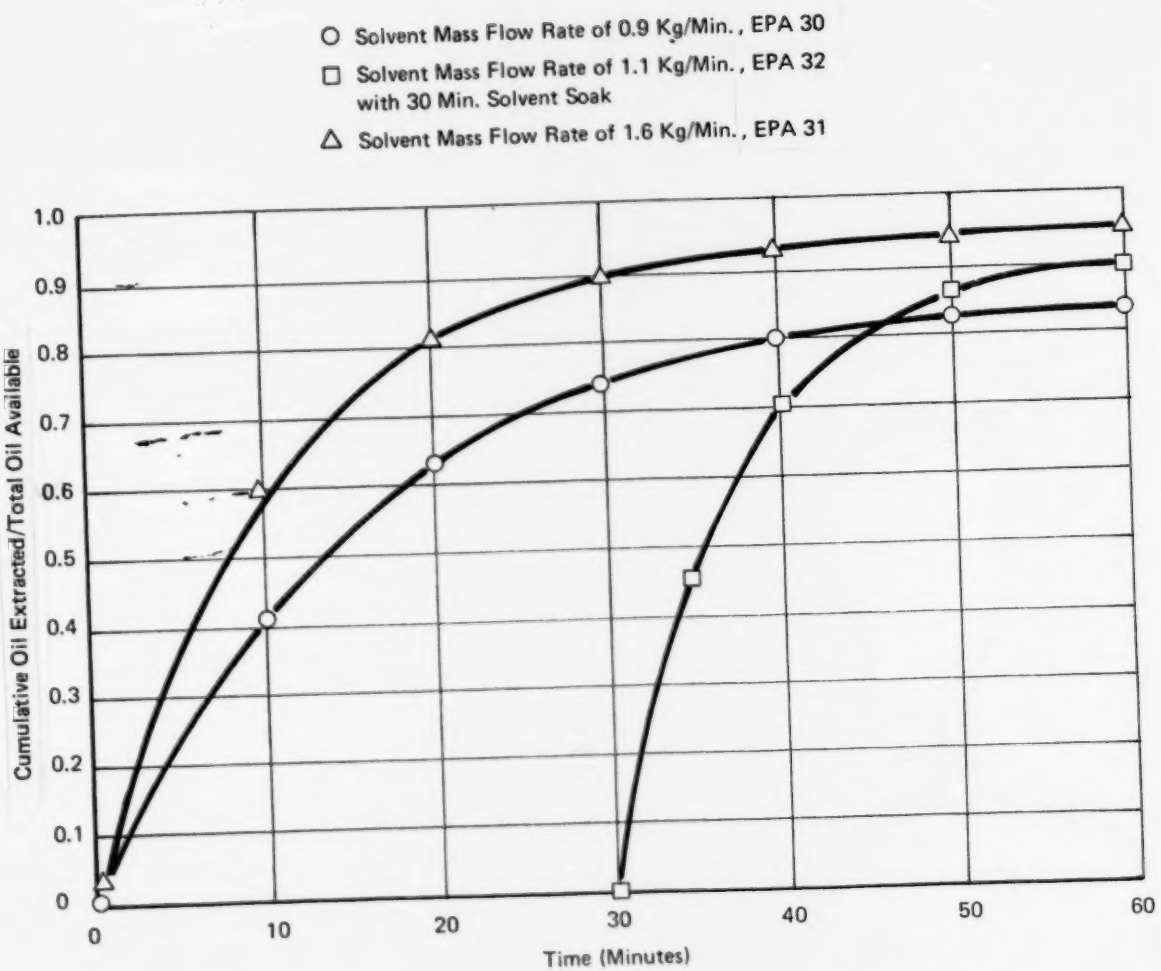

FIGURE 14 CUMULATIVE OIL EXTRACTED FROM MILL SCALE AS A FUNCTION OF TIME

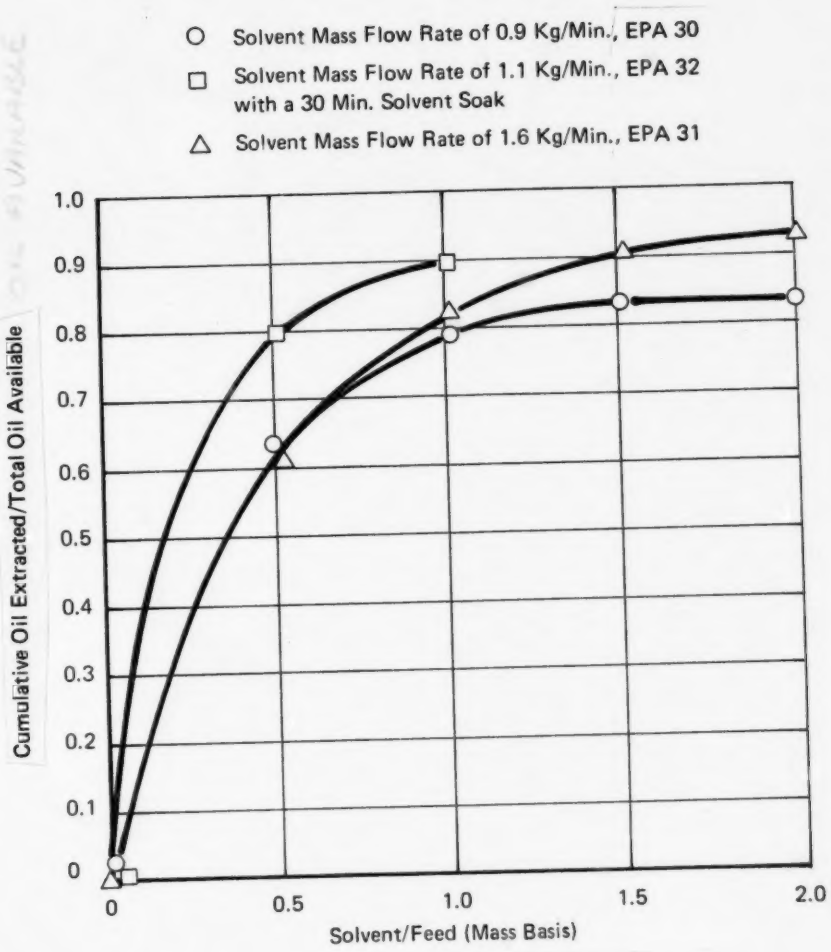

FIGURE 15 CUMULATIVE OIL EXTRACTED FROM MILL SCALE AS A FUNCTION OF SOLVENT-TO-FEED RATIO

Bleaching Clay

The results of feed and residue analyses is presented in Table 8 along with the run conditions for eight bleaching clay extractions. The first item of note is the much higher oil content of the clays when compared to mill scale. Much more oil is available per kilogram of feed stock. Also notable is the oil reduction efficiency. It is apparent that the bleaching clays will require much higher solvent to feed ratios and longer contact times to achieve complete extraction.

The highest oil reduction was observed in Run 56, a downflow run at low flow rate with an initial soaking period. The total contact time was nearly 5.5 hours. The average extraction reduced the oil content by 37% and took 2.5 hours. This level of reduction was also achieved in Run 55 in one hour, with no soaking, at a higher flow rate (0.82 Kg/min). This suggests that a higher flow rate enhances oil removal, but the optimum oil removal for these experiments occurred at flow rates between 0.33 and 0.44 Kg/min. Figure 16 is a graph of oil reduction efficiency vs. total contact time. It also distinguishes between up and down flow extractions. On this graph we see the upward trend in oil reduction efficiency with time in both upflow and downflow experiments. In all cases downflow is superior to upflow. The reason for this lies in the possibility of a channeling effect.

In an upflow pattern, the solids bed is more able to shift as the solvent flows through. It is possible that a channel of partially extracted clay could form. This partially extracted clay would present less resistance to incoming solvent, so more solvent would go through the channel, extracting the channel contents further. Unless the bed was disturbed and the solids redistributed (by pulsing the flowrate to fluidize the bed) the channel would direct flow away from oil laden clay and result in a poor extraction.

TABLE 8

BLEACHING CLAY FEED AND RESIDUE SOXHLET (OIL) ANALYSES, RUN CONDITIONS, AND OIL REDUCTION EFFICIENCIES

RUN	51	52	53	54	55	56	57	58
FEED OIL (Mass %)	24.7	17.4	18.7	18.6	18.4	20.2	22.5	16.1
MOISTURE (Mass %)	1.3	2.0	1.3	1.9	2.5	1.5	0.9	2.3
RESIDUE OIL (Mass %)	18.6	11.3	16.0	11.7	11.6	7.8	10.6	9.9
MOISTURE (Mass %)	0.9	1.5	1.2	1.7	1.7	1.4	0.9	1.5
SOLVENT MASS FLOWRATE (Kg/Min.)	0.77	0.91	1/31	0.35	0.82	0.33	0.44	0.15-1.36
SOLVENT-TO-FEED RATIO	5.2	4.0	6.3	3.1	3.7	7.8	5.6	5.0
TIME FOR EXTRACTION[a] (Min.)	125	103[b]	52[c]	107[d]	60	277[e]	172[f]	144
DIRECTION	UPFLOW	UPFLOW	UPFLOW	DOWN	DOWN	DOWN	DOWN	CROSS/DOWN/CROSS
OIL REDUCTION EFFICIENCY[g] (%)	24.7	35.1	14.4	37.1	37.0	61.4	52.9	38.5
TOTAL CONTACT TIME	125	161	112	148	60	322	197	144

[a] Extraction time does not include soak period.

[b] 58 Minute Soak

[c] 50 Minute Soak

[d] 41 Minute Soak

[e] 45 Minute Soak

[f] 25 Minute Soak

[g] (Feed oil content - Residue oil content) divided by Feed Oil Content

TABLE 9

BLEACHING CLAY MASS BALANCES

RUN	51	52	53	54	55	56	57	58
MASS CHARGED (A.R.)[1] kg	15.6	14.5	11.5	11.4	11.2	11.6	13.2	12.8
SOLIDS[2] kg	11.6	11.7	9.2	9.1	8.9	9.1	10.2	10.5
OIL[2] kg	3.8	2.5	2.1	2.1	2.0	2.3	2.9	2.0
MOISTURE[2] kg	0.2	0.3	0.2	0.2	0.3	0.2	0.1	0.3
RESIDUE RECOVERED (A.R.)[1] kg	13.4	13.6	10.7	10.1	10.4	10.0	11.7	11.2
SOLIDS[2] kg	10.8	11.9	8.9	8.7	9.0	9.1	10.4	9.9
OIL[2] kg	2.5	1.5	1.7	1.2	1.2	0.8	1.2	1.1
MOISTURE[2] kg	0.1	0.2	0.1	0.2	0.2	0.1	0.1	0.2
SOLIDS RECOVERY RATIO[3]	0.93	1.02	0.97	0.96	1.01	1.00	1.02	0.99
EXTRACTION EFFICIENCY[2,4] (%)	34	40	19	43	40	65	59	45
TOTAL OIL COLLECTED[5] kg	1.6	0.9	1.1	0.2	0.8	1.0	1.0	0.9
OIL RECOVERY RATIO[6]	1.2	0.9	2.8	0.2	1.0	0.7	0.6	1.0

- - - - - - - - - -

[1] A.R. - As Received

[2] Based on Soxhlet and Moisture Analysis on Feed and Residue

[3] Dry Solid Residue Recovered ÷ Dry Solids Charged

[4] [(Oil in Feed - Oil in Residue) ÷ Oil in Feed] x 100

[5] Calculated Amount Based on Reboiler Contents Plus Accumulation in Product Receiver

[6] Total oil collected ÷ (Oil in Feed - Oil in Residue)

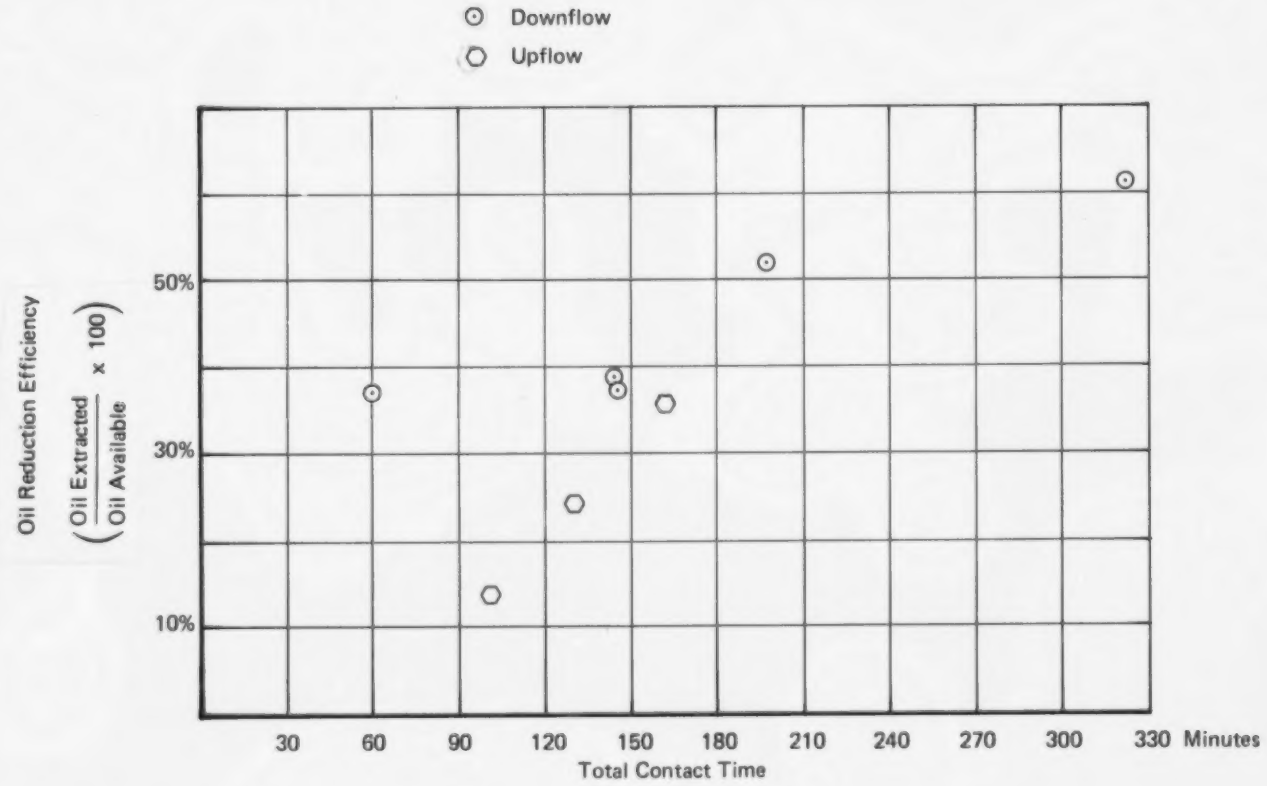

FIGURE 16 OIL REDUCTION EFFICIENCY vs. TOTAL CONTACT TIME FOR BLEACHING CLAYS

The overall lower oil reduction efficiencies for bleaching clays (when compared to mill scale data) may be attributed to the nature of the feed. Bleaching clay is a very fine, pourous material. The presence of fine pores throughout the particle adds another term to the overall mass transfer coefficient of oil from the particle to the solvent. In addition to particle-to-solvent mass transfer through the boundary layer of the individual particle, there exists an intra-particle diffusional resistance. The oil trapped in internal pores must diffuse through the particle matrix in order to be extracted. This resistance term will be independent of flow conditions as long as the oil at the particle boundary layer is removed as fast as the internal pore diffusion brings oil to the particle surface.

The mass balances for eight bleaching clay extractions are presented in Table 9. As in the mill scale data, the masses of feed and residue are broken up into their components of solids, oil, and moisture using laboratory data from moisture and soxhlet analyses. Comparison of dried solids into the bed to dried solids out of the bed is shown as solids recovery. In all cases, recovery was above 0.90, and above 0.96 for six of the eight runs.

A likely cause of the discrepancies lies in the dusty nature of the residue. Every effort at complete collection was made, but if the column was emptied too quickly, then a dusty cloud could form, the mass of which could not be determined. Material from such clouds was allowed to settle and was subsequently swept up and added to the residue, but the potential for loss of material was still present.

Oil recovery for an individual run proved difficult even with the larger masses of oil involved in the bleaching clay extractions. The same problems encountered in mill scale oil

determinations were encountered in the bleaching clay work. The mass of oil in the reboiler was difficult to determine accurately (see Appendix A). The lower flowrates used may have allowed oil buildup in the process equipment ahead of the reboiler. An amount of oil was removed from the system with each run, however, so a major component of the total oil collected was a measurable quantity. With the exceptions of Runs 53 and 54, oil recoveries ranged between 0.6 and 1.2, with an average recovery of 0.9.

Figures 17 and 18 plot the concentration of oil in the extract stream against contact time and solvent-to-feed ratio, respectively. With bleaching clays we see a gradual increase in oil content that comes to a maximum after about one hour of contact. This is in sharp contrast with the mill scale behavior of an immediate peak on flow initiation, but is not surprising in light of the adsorptive nature of the feed.

The bleaching clay was not saturated with oil to start with and so could be expected to act as a chromatographic packing. The oil would elute from the column in a broad band due to adsorption and desorption of the oil onto/from the "packing" (bleaching clay).

Figure 18 plots the concentration of oil in the extract stream as a function of solvent-to-feed ratio. This graph shows that the rate of extraction depends almost exclusively on solvent-to-feed ratio. All curves, with the exception of Run 58, show nearly identical oil buildup in the extract, and all curves share the same decay.

The effect of soaking can be seen by comparing the curve for Run 57 (a 25 minute pre-soak period) to Runs 54 and 56 (each approximately 45 minutes). The longer pre-soak period led to an

initially higher oil level, but this was offset by a somewhat quicker decline. The jog in the curve of Run 58 is a result of a brief period of crossflow extraction. It was hoped that by disturbing the flow pattern mid-run an increase in extraction efficiency could be obtained. This was not the case, as a comparison of Runs 54 and 58 show. Total contact time and overall extraction efficiency match in both cases. The crossflow experiment appears only to have shifted the Run 58 curve (of Figure 18) to the right.

The area under the curves in Figures 17 and 18 were taken with the mass flow rates to generate graphs of cumulative oil extracted from bleaching clays vs. time (Figure 19) and solvent-to-feed (Figure 20). Examination of Figure 19 reveals the dependence on time seen in bleaching clay extraction. The starts of the curves are offset by the amount of time the charge was allowed to soak in a non-flowing extractor. These offsets tended to even out after about 1.5 hours. After this first 1.5 hours the curves merge. The slopes of the downflow runs (54, 56, 57) are very close despite the 40% increase in mass flow rate used in Run 57 over the flow rate of Runs 54 and 56.

The effect of the increased flow of Run 57 is seen in Figure 20. When cumulative oil extracted is plotted as a function of a solvent-to-feed, we see that a higher flowrate results in more solvent usage for a given level of extraction. Indeed, the most efficient solvent usage occurs at the lowest flowrate tested (0.33 Kg/min, Run 56).

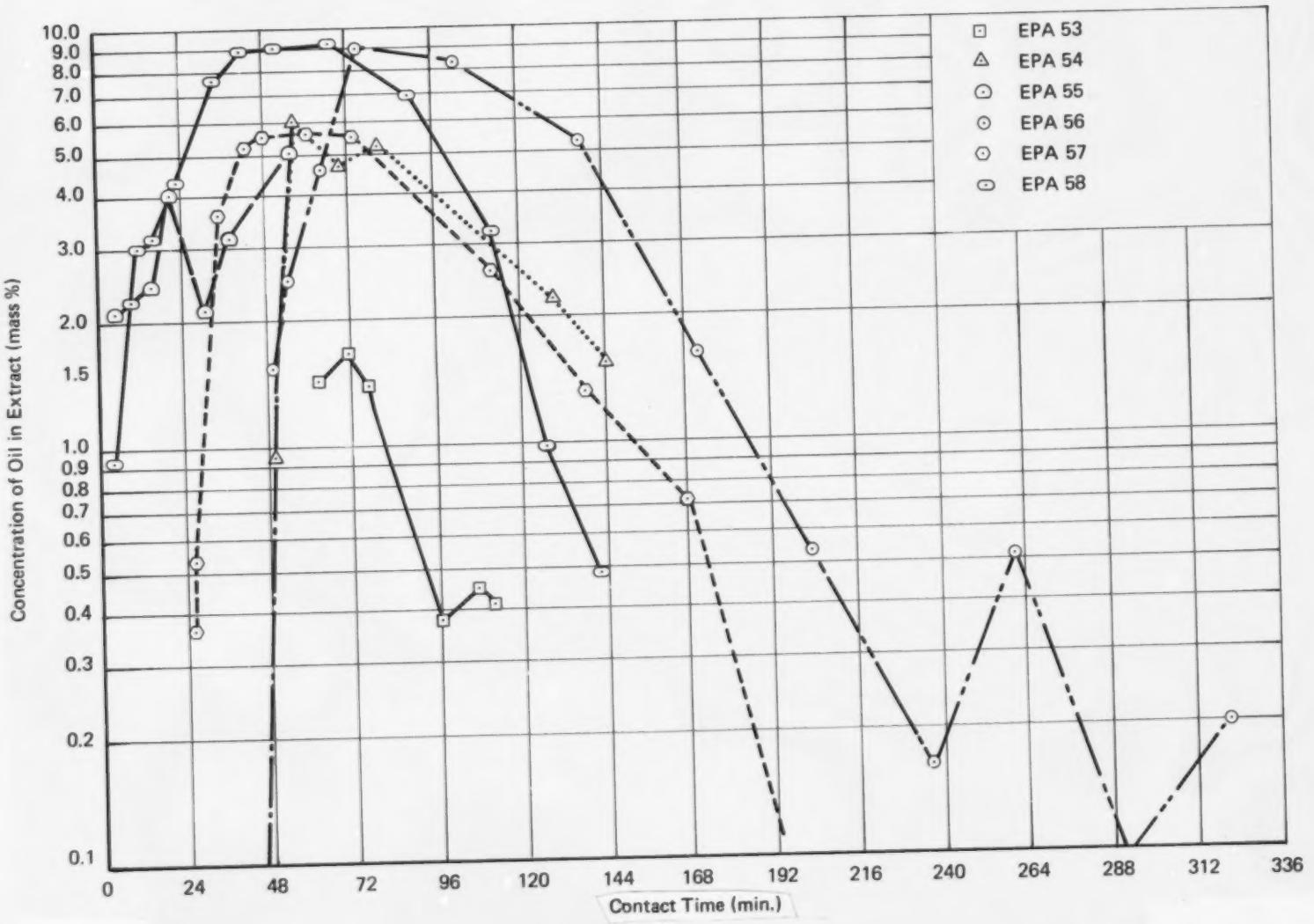

FIGURE 17 OIL IN BLEACHING CLAY EXTRACT AS A FUNCTION OF CONTACT TIME

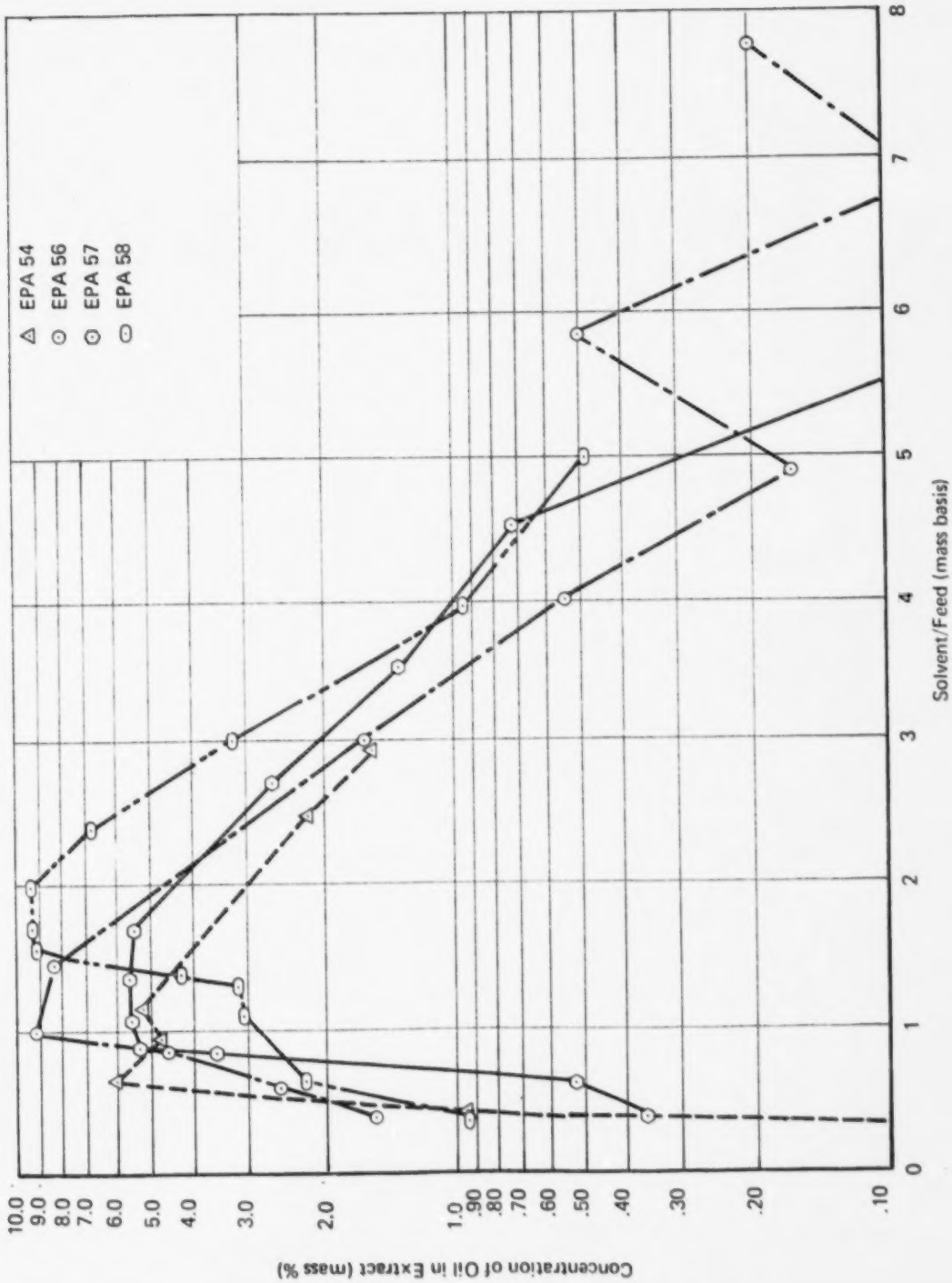

FIGURE 18 OIL IN BLEACHING CLAY EXTRACT AS A FUNCTION OF SOLVENT-TO-FEED RATIO

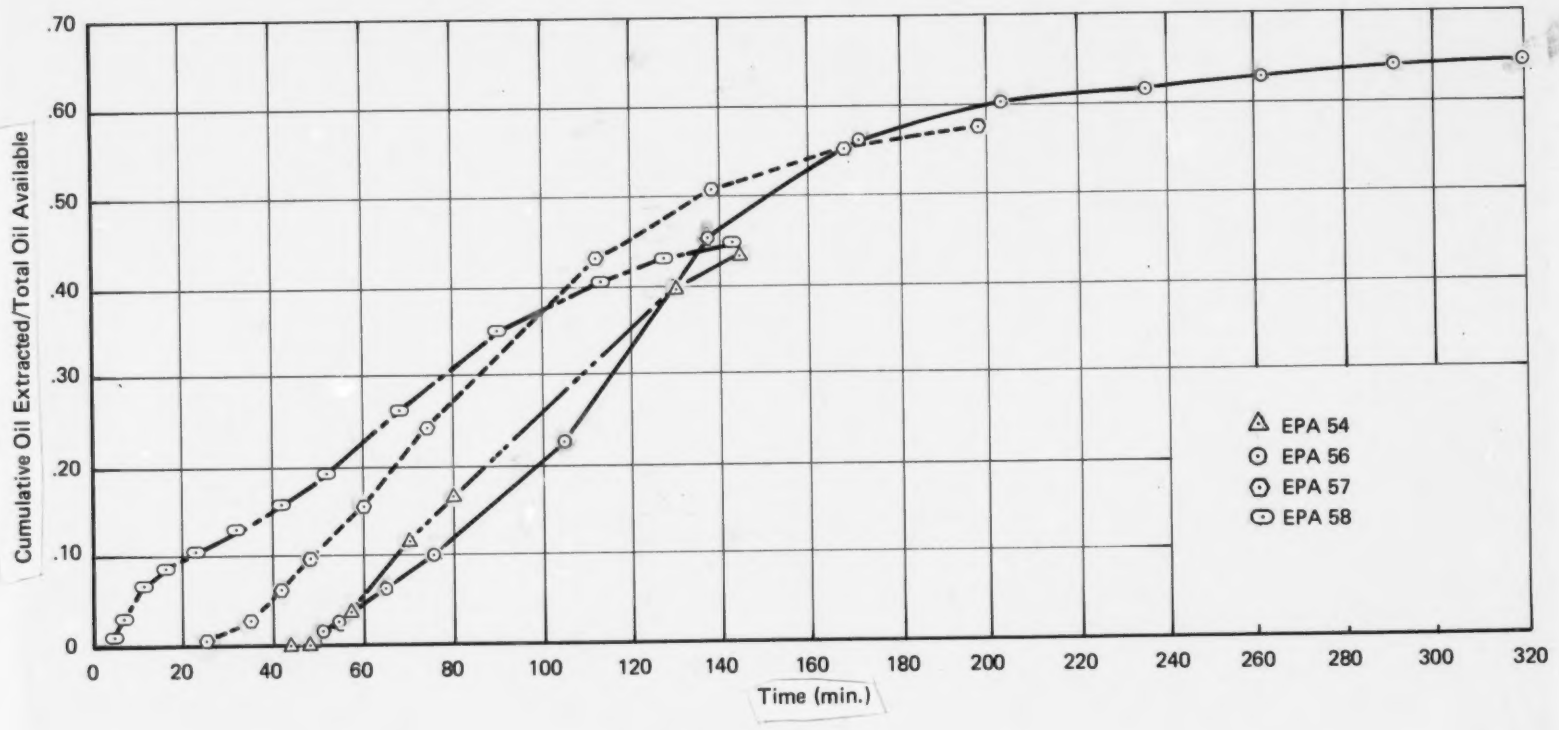

FIGURE 19 CUMULATIVE OIL EXTRACTED FROM BLEACHING CLAY AS A FUNCTION OF TIME

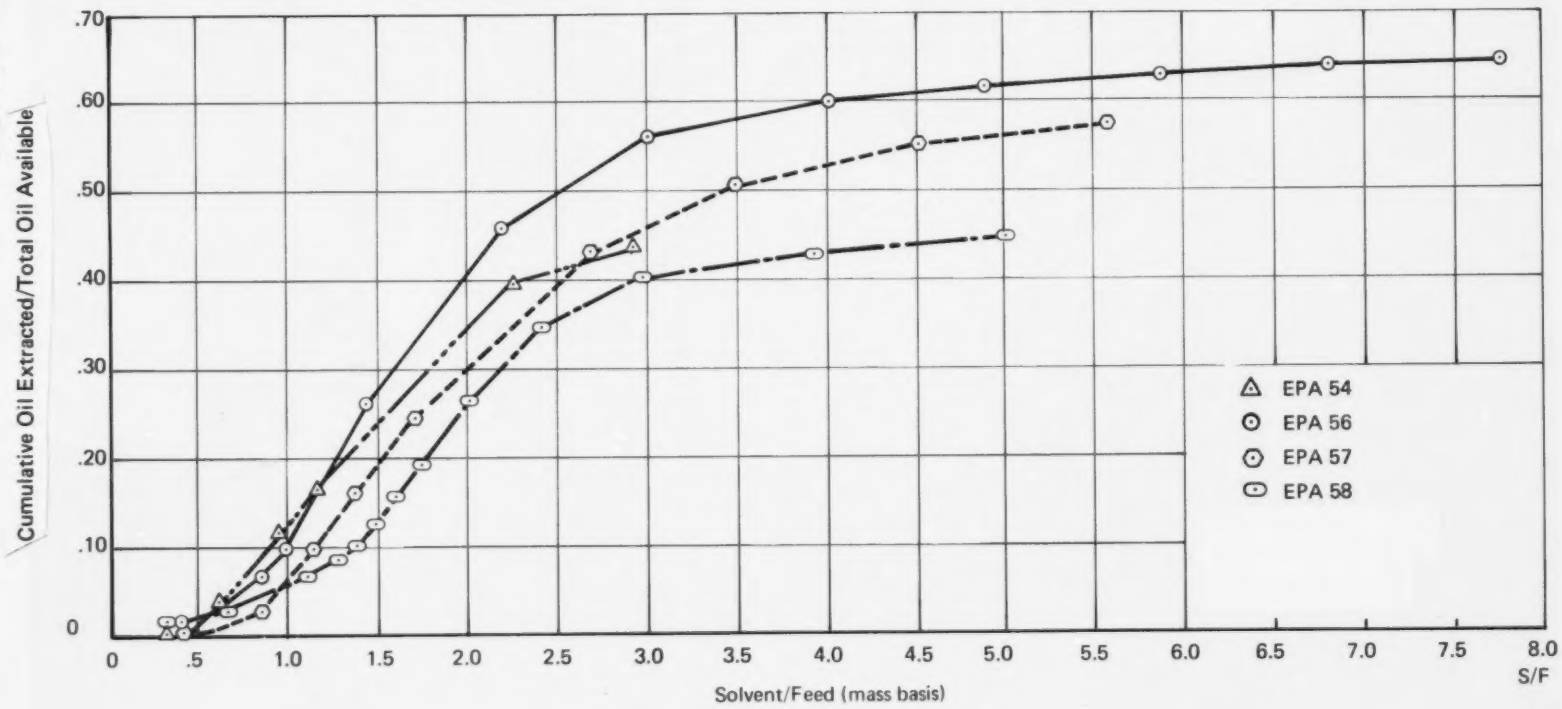

FIGURE 20 CUMULATIVE OIL EXTRACTED FROM BLEACHING CLAY AS A FUNCTION OF SOLVENT-TO-FEED RATIO

In order to investigate the possibility of channeling, a thorough study of the residue bed of Run 56 was conducted. Core samples were taken at the five points indicated in Figure 21. Each of these cores was divided into four height representative horizontal and vertical segment. Table 10 provides oil content (%) for each sample, as well as averages and estimated standard deviation (s) for each horizontal and vertical segment.

Observed values run from a low of 5.8% oil for the upper/middle sample of the inlet core to a high of 9.1% for the bottom sample of the center core. From this table we can see no gross evidence of channeling. A "dead spot" at the bottom of the center core is observed, but it is possible that this point was below the exit port and out of the direct flow pattern.

We also do not see a chromatographic effect in these data. All values are within two standard deviations of the average value. The oil does not appear to be desorbing and adsorbing as it is carried down the column; there is no evidence of a oil peak moving down the column. This was, however, an extended run. Surface oil could have been quickly removed (as evidenced by the shape of the curves in Figures 17 and 18) followed by a slower leaching process extracting the occluded and adsorbed oil. This two-step process fits well with the evidence of Figures 17 and 18 and the data of Table 10.

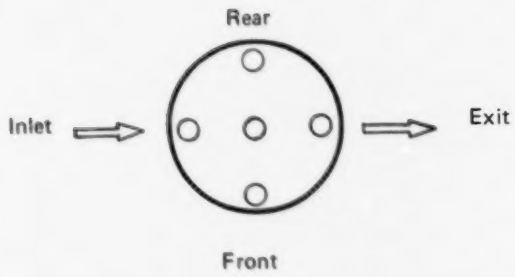

FIGURE 21 CORE SAMPLE DISTRIBUTION ACROSS EXTRACTOR

TABLE 10

OIL CONTENT OF SAMPLES TAKEN FROM VARIOUS POINTS IN A BLEACHING CLAY BED AFTER EXTRACTION

(Mass Percent)

	INLET	REAR	CENTER	FRONT	EXIT	AVERAGE
TOP	6.16	7.71	7.67	7.29	6.95	7.16 S = 0.64
UPPER MIDDLE	5.81	7.16	5.65	6.90	7.25	6.55 S = 0.77
LOWER MIDDLE	6.00	6.68	8.28	6.72	7.87	7.11 S = 0.94
BOTTOM	7.34	7.29	9.07	8.13	7.54	7.87 S = 0.75
AVERAGE	6.33 S = 0.69	7.21 S = 0.42	7.67 S = 1.46	7.26 S = 0.63	7.40 S = 0.39	7.17 S = 0.86

VI. PRELIMINARY ECONOMIC ANALYSIS

Mill Scale

A preliminary design was prepared for a mill scale de-oiling plant for the purpose of a process feasibility study. The design criteria for this plant are presented in Table 11. The plant was designed to process 80,000 metric tons of mill scale per year. The process will run concurrently with other steel mill operations, and thus is designed to be built "mill-worthy"; i.e., capable of year round, 24 hour per day operation. A feed oil content of 5% was used in the design basis; industry contacts indicated that would be representative of fresh oily mill scale and that the low feed oil contents observed in our testing was lower than average.

The process conditions for the design basis use a solvent-to-feed ratio of 2 to 1, and include a 30 minute soak period. Total process time, including loading, soak, extraction, and unloading, is 75 minutes. A high flow rate coupled with the soak will provide the required level of de-oiling. The solvent recovery system recovers 99.98% of the process solvent; only small quantities of solvent are lost with the scale and oil.

Equipment costs are listed in Table 12 and overall capital costs in Table 13. Operating costs are shown in Table 14 as are credits for recovered oil and for recyclable mill scale.

The recovered oil is valued as heating fuel; the value will be higher if the oil can be reused as lubricant. The recovered mill scale is valued at $14 per metric ton by industry. A full credit is taken for this mill scale since without processing the

mill scale is a waste product that is usually stockpiled or otherwise disposed of. The cost of this disposal has not been taken into the calculation as a credit. The current disposal method, stockpiling, incurs no expense (except the cost of the land and associated taxes). This low disposal cost is subject to change as more stringent storage and disposal regulations are implemented by EPA.

It can be seen from these tables that a net annual income of $965,240 will be realized from the installation of this process. Comparison of this value with the capital costs shows a net payout of 23 months. In addition, the environmental problems associated with stockpiling oily scale will be eliminated. This process will handle both fresh material from the mill and oily mill scale previously stockpiled.

TABLE 11

MILL SCALE DE-OILING PLANT DESIGN CRITERIA

Plant Capacity:	80,000 mcton/year
Operating Factor: (350 days/year, 24 hr/day, 7 days/week)	8400 hours/year
Feed Conditions	
Oil Content:	3-6% (5% avg.)
Moisture:	5-10% (7% avg.)
Solids:	Balance
Temperature:	10-38C
Particle size:	-325 to +4 mesh
Product Quality	
Oil content:	0.1%
Moisture:	5-10%
Solids:	Balance
Product Recovery	
Oil:	> 95%
Solids:	> 99%
Solvent:	Solvent-12
Solvent-to-Feed Ratio:	2
Solvent Recovery:	99.98%
Extraction time per Batch: (Including loading, unloading, soak period.)	75 minutes
Extraction Conditions:	21-27C 700-800 kPa

TABLE 12

MILL SCALE DE-OILING PLANT
EQUIPMENT COSTS

Extraction columns (2):	$100,000
Compressors:	
200 HP	125,000
25 HP	50,000
Solvent Stripper:	20,000
Heat Exchangers:	88,000
Decanter, Flash, & Separator Drums:	56,000
Pumps (4):	18,000
Tanks and Bins (2):	20,000
Solids Handling Equipment:	15,000
	$492,000

TABLE 13

MILL SCALE DE-OILING PLANT
CAPITAL COSTS

Civil and Structural Work	$100,000
Auxiliary Construction Work	72,000
Lab Equipment and Furniture	20,000
Plant Equipment	492,000
Plant Piping	133,000
Offsite Piping	20,000
Electrical Work	74,000
Instrumentation	123,000
Plant Equipment Installation Costs	350,000
Engineering	200,000
Expense Items	20,000
Contingencies (@15% of total cost)	250,000
	$1,854,000

TABLE 14

MILL SCALE DE-OILING PLANT

CAPITAL COSTS

Labor (1 Operator/Shift @ $24/hr)	$ 210,240
Supervision: (1/2 Supervisor @ $36/hr, day shift only)	37,400
Electricity (2.3 E6 kw-hr/yr @ $0.075/kw-hr)	172,000
Cooling Water: (41,700 cubic meters @ $0.058/cubic meter)	2,420
Solvent Make-Up (32,000 kg/yr @ $2.20/kg)	70,400
Maintenance (4% of Capital Investment)	74,200
Taxes and Insurance (2% of Capital Investment)	37,100
Depreciation (10% of Capital Investment)	185,000
Total Annual Operating Cost	$ 788,760
Credit on Recovered Oil: (5% oil content feed, 3,900,000 kg @ $0.176/kg)	($ 690,000)
Credit on Recovered Mill Scale: (76,800 metric tons @ $14/metric ton)	($1,064,000)
Annual Operating Income	$ 965,240

Bleaching Clay

A preliminary design for a bleaching clay/vegetable-oil extractor has been prepared based on the pilot plant data. A continuous countercurrent extractor was coupled with the vapor recompression system. The design basis is listed in Table 15.

The countercurrent extractor was chosen to eliminate potential channeling problems associated with fixed bed operation. From the lab experiments, a 5-hour contact time was required to achieve the desired level of extraction.

It is seen that the major expense is labor. A full-time operator has been assigned to this plant; a part-time may be all that is required. It is seen that the processing cost is 10 cents per kilogram of feed.

Table 18 shows the credits that this plant can be expected to generate. Only credits for recovered oil and for reduced disposal costs were taken. It may be possible to recycle some percentage of the de-oiled clay, thus creating another credit. Even without this credit it can be seen that the net payout for this plant is 17 months.

TABLE 15

BLEACHING CLAY DE-OILING PLANT
DESIGN CRITERIA

Plant Capacity (430 kg/hr)	3,612,000 kg/yr
Operating Factor: 7 day/week, 3 shifts/day, 50 wks/yr	8,400 hours
Feed Conditions	
Oil Content:	35%
Moisture:	2%
Solids:	Balance
Temperature:	25C
Particle Size:	< 200 Mesh
Product Quality	
Oil Content:	5%
Moisture:	2%
Solids:	Balance
Solvent:	Solvent-12
Solvent-To-Feed Ratio:	3:1
Solvent Recovery:	99.75%
Extraction Time:	5 Hours
Extractor Conditions	
Temperature:	25 C
Pressure:	750 kPa

TABLE 16

BLEACHING CLAY DE-OILING PLANT CAPITAL COSTS

Extractor:	$100,000
Solids Conveyors (2):	15,000
Pumps:	5,000
Compressors (2):	35,000
Heat Exchangers (5):	7,000
Tanks and Bins:	40,000
Hardware Total	$202,000
Engineering, Site Preparation, Assembly, Installation	505,000
Total Capital Cost (Hardware Cost X 3.5)	$707,000

TABLE 17

BLEACHING CLAY DE-OILING PLANT OPERATING COSTS

Labor:	
(1 Operator/Shift @ $15/hr)	$126,000
Electric Power:	
(344,400 Kw-hr/yr @ $0.075/Kw-hr)	25,800
Cooling Water:	
(79,000 m^3/yr @ $0.058/$m^3$)	4,600
Refridgeration:	
(10 ton/day @ $1.50/ton)	5,200
Steam:	
(36 kg/hr @ $22/1000 kg)	6,700
Make-Up Solvent:	
(19,500 kg @ $2.20/kg)	42,900
Maintenance:	
(4% of Capital Investment)	28,300
Taxes & Insurance:	
(2% of Capital Investment)	14,100
Depreciation:	
(10% of Capital Investment)	70,700
Total Annual Operating Costs	$324,300
Processing Cost Per Kilogram	$0.10/kg

TABLE 18

ANNUAL CREDITS FOR OPERATION OF BLEACHING CLAY DE-OILING PLANT

Value of Recovered Oil: (1,083,600 kg @ $0.44/kg)	$ 477,000
Reduced Disposal Costs: ($110/meton for oily wastes vs. $22/meton for de-oiled wastes)	$ 341,000
Total Credits Per Year:	$ 818,000
Payout:	17 Months

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2. Francis, A.W., J. Phys. Chem. 58 1099,(1954)

3. Sevne, J.C., and Wilson, K., "The Use and Fate of Lubricants, Oils, Greases, and Hydraulic Fluids in the Iron and Steel Industry", Report EPA-600/2-78-101, May 1978.

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APPENDIX A

QUALITY CONTROL EVALUATION REPORT

I. SUMMARY

Purpose of Project

The purpose of this project was to evaluate the feasibility of using condensed gas solvents to extract oil from industrial waste samples, and to provide preliminary engineering data and experience necessary for the design and operation of full scale plants. The waste streams selected for study were:

1. oily steel mill scale, a by-product of steel production, and
2. oil-laden bleaching clays, a waste stream from vegetable oil production.

Purpose of the Quality Control Evaluation Report (Q.C.E.R.)

This appendix comprises a Q.C.E.R. on this project and as such reports on the data quality and research results in terms of precision, accuracy, completeness, and reproducibility, as well as a semi-quantitative assessment of the results and conclusions.

II. OVERALL EVALUATION

A quality assurance project plan was not submitted prior to this project. As a result, no formal quality control program was in effect during these experiments. However, in the three major areas of data generaton (Appendix A, Section II), calibration procedures, analysis of prepared standards, and material balance comparisons were routinely used to evaluate the accuracy of results. A summary of the data taken and the procedures used to determine reliability appears in Table A-1. Also presented in this table is the maximum error in accuracy of any of the individual measurements reported.

TABLE A-1

OVERALL ACCURACY OF DATA COLLECTED FOR BLEACHING CLAY AND MILL SCALE SAMPLES

DATA COLLECTED	UNITS OF MEASUREMENTS	METHOD OF DETERMINATION	RELIABILITY TEST	ERROR BL CLAY	ERROR MSCALE
Feed and Residue Mass	Kg	Weighing on Platform Balance	Calibration Weight/ Manufacturer Specification	±1%	<1%
Solvent Flow Rate	Kg/Min	Measurement By Liquid Flowmeter	Calibration with Water/ Manufacturer Specification	±0.4%	
Feed and Residue Moisture Content	Mass Percent	Oven Drying, Mass Determination on Laboratory Balance	Balance Calibration	±50%*	
Feed and Residue Oil Content	Mass Percent	Soxhlet Bench Scale Extraction	Balance Calibration and subsequent investigation using prepared standards.	7.5%	

* Not including sampling errors.

The least accurate data are the moisture analysis and the oil content of feeds and residues. This is due to the low values of moisture observed for all samples (typically <3%) and the low oil contents of mill scale feeds and residues. A determination of the accuracy of the soxhlet technique when applied to bleaching clays (typical feed oil content of 35%) showed that these data are within 0.78 mass percent of a true value. A similar degree of accuracy is expected of mill scale analyses, but this value can represent more than twice the amount of oil observed in these samples. Reproducibility, therefore, must be taken as more important than absolute accuracy in the case of mill scale.

III. DATA GENERATION AND ERROR ANALYSIS

The results presented in this report are based on three principal sets of data:

- Feed and Residue Mass
- Feed and Residue Oil Content
- Solvent Stream Oil Content

A fourth set of data, the amount of oil collected in an extraction, was used as a check on the closure of the mass balance for a given run. The first two sets of data, feed and residue masses and oil contents, were used to determine the overall efficiency of an extraction run (Tables 6 through 9). The third set of data, the solvent stream oil content, was used to prepare the graphs of Figures 12 through 20.

Feed and Residue Mass Analysis --

The procedure for mass determination has already been described (Section IV). The balance used had a one ounce readability, and all weighings were done by difference. A one ounce error represents an average error of 0.2% for mill scale and 0.5% for bleaching clays. This error applies to feed measurements for both material; transfer into the extractor was always completed with one charge of our transfer vessel.

Residue mass error analysis for mill scale is identical to feed mass analysis in the case of mill scale. The material was easily removed from a column and quantitatively collected in a weighed receiver vessel. No residue was observed on the column walls, and no material was lost to the floor. This was not the case for bleaching clays.

The removal of bleaching clay residue from an extractor column routinely entailed the use of rods to loosen up the bottom of the bed and to start the flow of solids out of the extractor. These solids were very fine and dusty in nature, and would generate a dust cloud during the emptying procedure. This cloud would be allowed to settle and would be swept up and added to the residue bulk, but complete residue collection remained uncertain. Solids recovery (Table 8) indicates that the amount escaping collection could be, at worst, 1.0 kg, or 6.3% of the initial clay charged. This assumes no error in residue oil and moisture analysis. The level of clay collected by sweeping was always under 0.5 kg, indicating that an unnoticed loss of 1 kg was highly unlikely. It is more likely that an error in oil analysis was responsible for discrepancies in solids recovery.

Feed and Residue Oil Content Analysis and Errors —

The oil content of feeds and residues were routinely determined by exhaustive soxhlet extraction1 of a pre-dried solid sample using an appropriate solvent (solvent-113, petroleum ether). The solvent was evaporated in a vacuum oven at 60 C to dryness, and the dry de-oiled residue mass divided by the initial dry, oily solid sample mass to obtain a mass percent of oil. This method has been designated by the American Oil Chemists' Society as the most reliable (AOCS stated precision $\pm$0.47 mass %), and is the most commonly used method for vegetable oil extraction2.

A program was initiated to determine the precision and accuracy of the soxhlet extraction technique when applied to bleaching clays. The results of this program are presented in Tables A-2 and A-3.

We see in Table A-2 an average absolute error of 0.47%. This indicates the possibility of irreversible adsorption of oil onto the bleaching clay, or perhaps the adsorption of a non-extractable oil impurity. We also see from this table an average extraction of 0.19% from a blank (no oil) sample of clay. This is a result of impurities in the solvent or of extractables in the thimble sample holders.

Table A-3 shows repeated analysis of a single sample of bleaching clay. A statistical analysis of this data results in a standard deviation of 0.531, and an 0.95 probability that the values are within 1.06 mass percent of the mean value.

1USEPA, Manual of Methods for Chemical Analysis of Water and Wastes, p. 226, EPA-625/6-74-003, 1974

2Meldenhahl Analysis of Fats and Oils, p. 15, The Gerard Press Publishers, Champaign, IL.

Although this analysis shows that the soxhlet technique is itself reliable, a larger problem may exist in methods used to collect samples for analysis. The feeds and residues could not be assumed homogeneous, so various techniques were used for feed and residue analysis. For feed samples, several aliquots were taken as the column was filled. These were combined and used for feed analysis. Residues were sampled using a cone and quartering technique. In all cases, a sample of less than one mass percent was taken as representative of the whole.

c. Solvent Stream Oil Content Errors

The curves of Figures 12 through 20 were generated using the data obtained by bomb sampling the extract stream leaving the extractor. This data requires three weighings on a mettler top loading balance (p1210) readable to 0.01 g. The maximum additive error could be $\pm$0.03 g. The total mass of solvent was either 40 or 12 grams (depending on sampler) resulting in a possible weighing error of, at worst, 0.25% in the value for the concentration of oil in solvent.

A mass of gas could have been dissolved in the oil, thus giving a high value for oil concentration in the extract stream. This error can be shown to be less than 1% of the oil content observed using Henry's Law, which states that the mole fraction of dissolved gas in a liquid solution is proportional to the partial pressure of that gas (approximately 1 ATM) divided by a constant.

$$x_a = P_a / H$$

where x_a = mole fraction of dissolved gas

P_a = partial pressure of dissolved gas

H = Henry's constant

TABLE A-2

ANALYSIS OF PREPARED STANDARDS TO DETERMINE ACCURACY

PREPARED OIL CONTENT OF STANDARDS	OIL CONTENT BY SOXHLET EXTRACTION	ERROR (mass %)	ERROR (%)
0 (clay + no oil)	0.26	0.26	-----
0 (clay + no oil)	0.12	0.12	-----
4.19	4.10	0.09	-2.1
4.75	4.68	0.07	-1.5
10.86	10.08	0.78	-7.2
10.55	10.06	0.49	-4.6
18.61	17.89	0.72	-3.9
21.60	20.95	0.65	-3.0

TABLE A-3

ANALYSIS OF CONTROL SAMPLES TO DETERMINE PRECISION

DATE	SOXHLET RESULTS (mass %)	DEVIATION*
9-04-84	19.53	0.77
9-10-84	20.84	0.54
9-16-84	20.10	0.20
9-16-84	20.30	0.00
9-16-84	20.75	0.45

*Mean Value = 20.30 mass %

A Henry's constant is not available for solvent-12, but for CO_2, $H = 1.25 \times 10^6$ (International Critical Tables, Vol. 3, p. 260, McGraw Hill Book Club, 1928). One can calculate a value for x_a equal to 0.061 mole percent. If we assume a molecular weight of oil at 1200 grams per mole, then this results in a value of 0.0061 mass percent solvent in oil. A conservative estimate for the Henry constant for solvent-12 as being an order of magnitude higher than that for CO_2 results in an error of less than 0.1 mass percent oil in solvent.

Yet a larger error does exist. Figures 16 and 17 have been normalized such that the end level of extraction achieved matches the degree of extraction calculated from feed and residue analysis. The raw curves are shown in Figures A-1 and A-2. These curves indicate final extraction levels approximately one-third higher than that actually achieved. It was felt that to reduce each curve to match the final extraction achieved would better represent the actual progress of the extraction and allow comparison between runs.

These curves are the result of multiplying the oil contents observed by the flowrate for that period of time. As previously discussed, the oil content value can be in error by less than 0.5%. This leaves only the mass flow meter responsible for the discrepancy between the raw curves and the calculated extraction efficiency.

The flow meter was calibrated periodically with water. The totalized mass throughput was found to agree within $\pm$0.2% to the amount (mass) of water used in the calibration at flow rates near those used for these experiments. No correction for solvent-12 was suggested by the manufacturer (Micro-Motion of Bolder, CO) as the meter is sensitive only to mass. At this time, the discrepancy is unresolved.

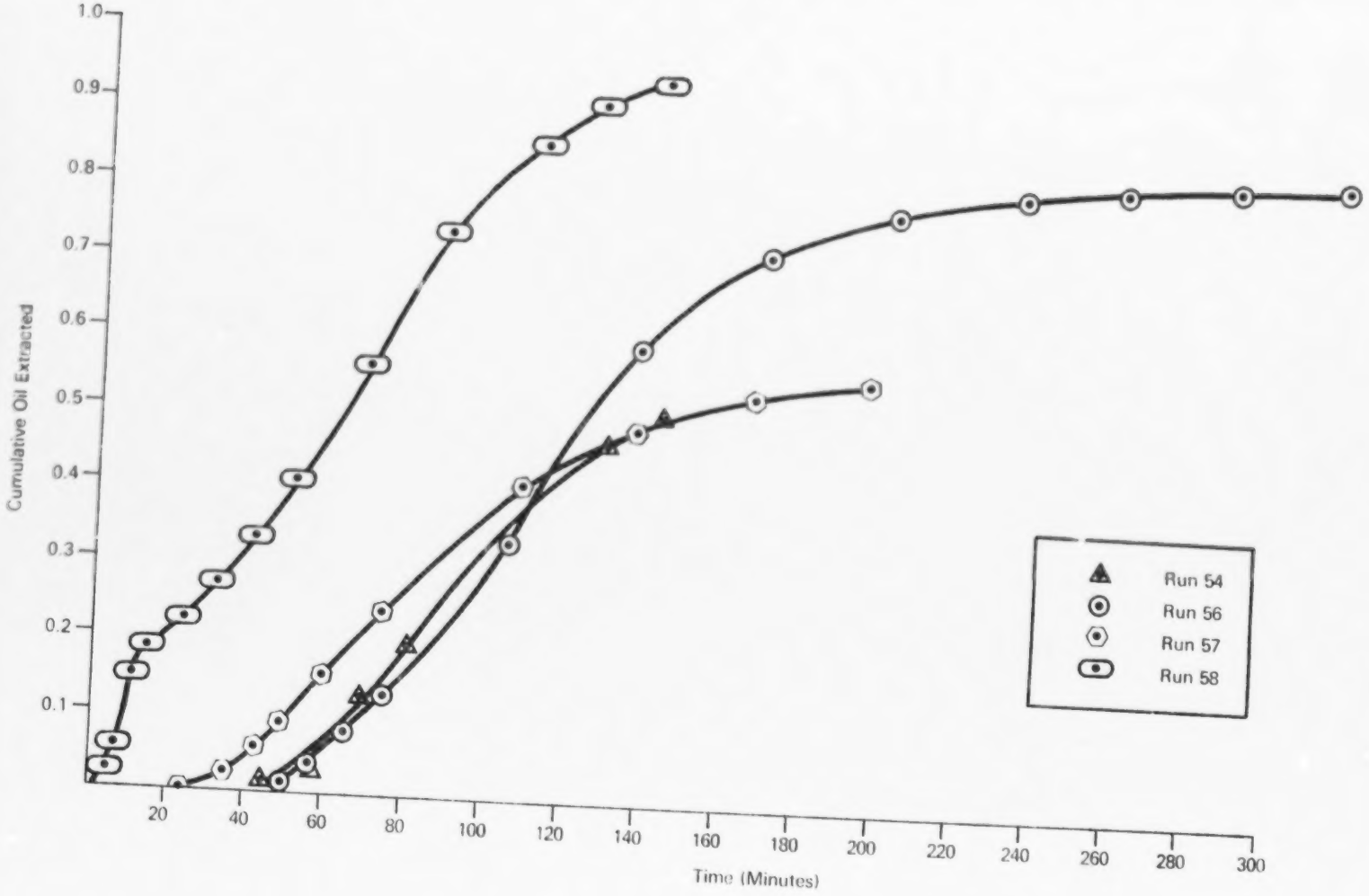

FIGURE A1 CUMULATIVE OIL EXTRACTED FROM BLEACHING CLAY VS. TIME (RAW DATA)

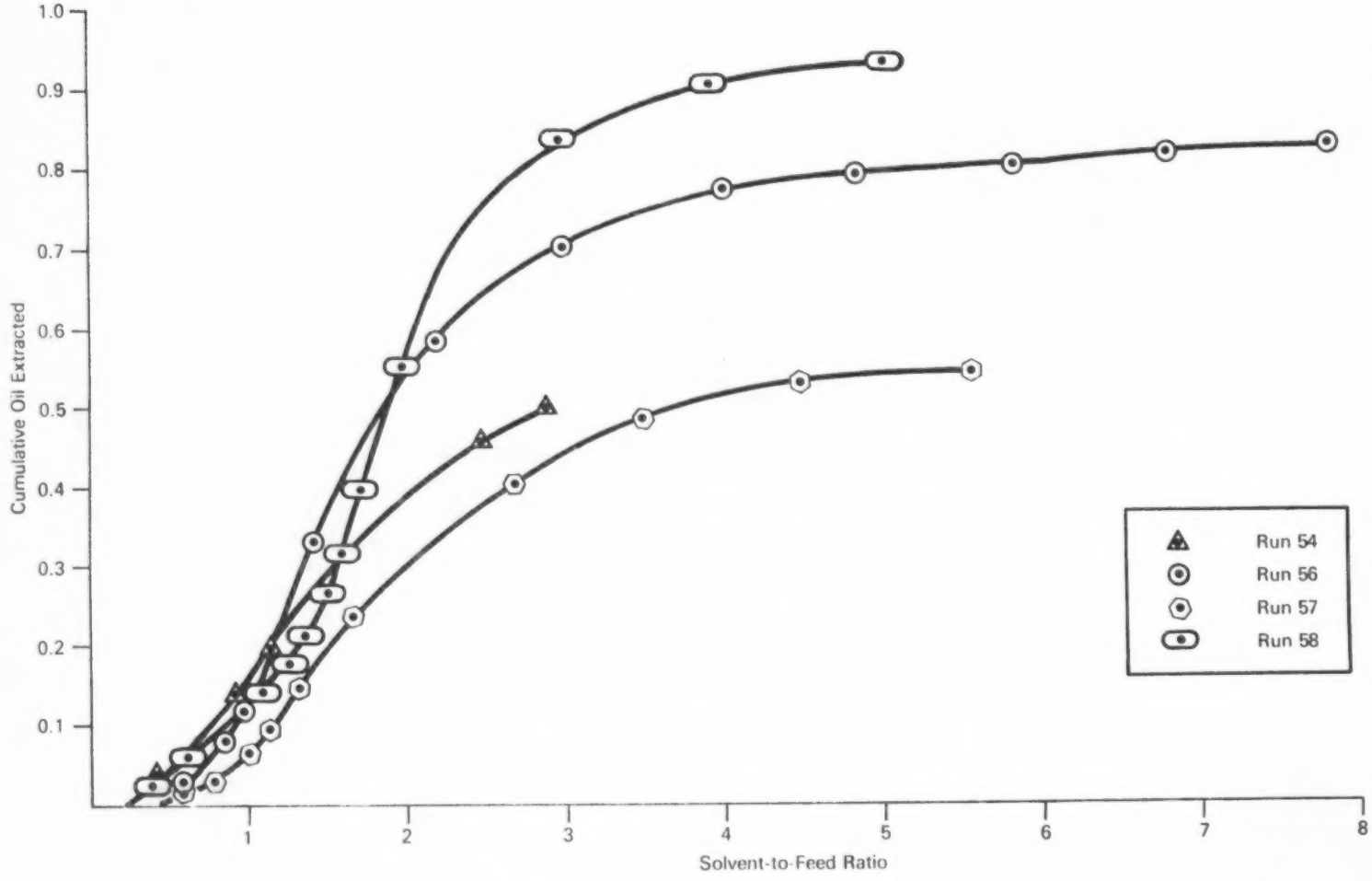

FIGURE A2 CUMULATIVE OIL EXTRACTED FROM BLEACHING CLAY VS. SOLVENT-TO-FEED RATIO (RAW DATA)

d. Extracted Oil Mass Error

The greatest inaccuracies observed in these experiments occurred in the measurement of the amount of oil collected during an individual run. This is seen in Tables 6 and 8 as a wide variation in oil recovery for individual experiments. The extraction system was not emptied of solvent after each run and so no absolute amount of oil extracted could be measured. A calculation scheme was employed to determine the oil contained in the system.

This calculation was dependent on three measurements:

a. the mass of oil gained in the product receiver;
b. the concentration of oil in the reboiler; and
c. the volume of solvent/oil solution in the reboiler.

The first measurement was performed using the platform balance previously described in this appendix. The one-ounce readability taken with the average 0.75 kg mass of oil collected results in a possible error of $\pm$4% in this measurement. This error would only apply to bleaching clays because the product receiver was not used during individual mill scale runs.

The remaining measurements were used to calculate the amount of oil in the extractor system. Two assumptions were made: first, that all the oil in the system was in the reboiler; and second, that the oil/solvent solution was well mixed throughout the reboiler. The uncertainty of these assumptions give rise to the uncertainty of the resultant mass calculation.

A degree of uncertainty exists in these remaining measurements. The concentration of oil in the reboiler required two weighings on an Ohaus Dial-O-Gram balance with 0.1 g

readability. The oil gained was typically five to ten grams. The resultant reading error could be 4% of the oil collected.

The solvent sampled in this procedure was measured by an American Meter Co. dry gas test meter. This meter was tested and found to have an accuracy of 2%. This was used in a division with the oil weight (4% uncertainty) yielding an overall uncertainty of 8%.

The reboiler volume was calculated based on the weight of liquid in a sight glass. This level was measured to $\pm$ 1 mm corresponding to $\pm$0.05 l of reboiler volume. The median volume of the reboiler unit is 8 l, giving an uncertainty of $\pm$0.6%. This value applies to the direct reading regime of the sight glass (Section IV). Where a calculated volume was employed. This error is buried by a systematic error (Figure 8) of 0.5 to 1 liter, or as much as 12.5% of the median reboiler volume. The calculation of reboiler volume was seldom required. A conservative estimate of $\pm$10% uncertainty for these data is reasonable.

A 10% level of uncertainty still does not cover the range of oil recoveries observed. A problem must exist in the assumptions on which the calculation is based.

The first assumption, that all oil is located in the reboiler, is flawed by the existance of a decanter located just before the reboiler. This unit acts as a phase separator in processes where there is significant amounts of water extracted with the oil. It also serves to collect solvent vapors resultant from the pre-still pressure letdown. The decanter sends these vapors to a high point on the still tower and sends the liquid on to the reboiler.

The volume of this decanter was six liters. An effort was made to run the system after the extraction for a long enough period to exchange the contents of the decanter with fresh solvent, but there was no way of knowing that complete exchange had occurred. Incomplete exchange would have resulted in underestimating the amount of oil in the system and an oil recovery value (Tables 6 and 8) below 1.

The second assumption, that the reboiler contents were well mixed, is generally a good one despite the static nature of the reboiler and the lack of mechanical mixing. In a partly full to full reboiler, thermal gradients and boiling should maintain homogeneity. The assumption breaks down if the reboiler contents become highly concentrated in oil by vaporizing more solvent than is coming into the reboiler. This results in a layer of oil at the bottom of the reboiler. Subsequent volume increases would "float" a layer of solvent on this oil that would only slowly approach homogeneity by diffusion.

Sampling from such a system (Figure 7) would result in a high value for the concentration of oil in the reboiler and so a high value for total oil collected. This is reflected by a value for oil recovery (Tables 6 and 8) above 1.

The amount of oil collected and the individual oil recovery of a run were used as a second check on mass balance (after dry solids recovery). Discrepancies in this check do not affect the overall conclusions of this report, but do point out the difficulties in measuring small changes in a large system.

IV. APPLICATION TO DESIGN

A worst case scenario has been prepared assuming a 100% error in the required solvent-to-feed ratio for the 3,612,000 Kg/yr bleaching clay plant presented in Section VI of this main report. For simplicity, the six-tenths factor rule was used to scale up new equipment costs. This rule states:

$$\text{Cost of Equipment A} = \text{Cost of Equipment B} \times \left[\frac{\text{Capacity of Equipment A}}{\text{Capacity of Equipment B}}\right]^{0.6}$$

Tables A-4 and A-5 show that by being off by a factor of 2 increases capital costs by 30% and operating costs by 20%.

TABLE A-4

SENSITIVITY OF CAPITAL COST TO
SOLVENT-TO-FEED RATIO:
IMPACT OF A TWO-FOLD INCREASE

Extractor:	$100,000	$151,600
Solids Conveyors (2):	15,000	22,700
Pumps:	5,000	7,600
Compressors (2):	35,000	53,000
Heat Exchangers (5):	7,000	10,600
Tanks and Bins:	40,000	60,600
Hardware Total:	$202,000	$306,100
Engineering, Site Preparation, Assembly, Installation:	505,000	764,900
Installed Cost:	$707,000	$1,071,000

TABLE A-5

SENSITIVITY OF OPERATING COST TO SOLVENT-TO-FEED RATIO: IMPACT OF A TWO-FOLD INCREASE

Labor: (1 Operator, $24/hr)	$126,000	$126,000
Electric Power: (74,000 kw-hr/yr @$0.075/kw-hr)	25,800	51,600
Make-up Solvent: (734 kg/yr @ $2.20/kg)	42,900	42,900
Maintenance : (4% of Capital Investment)	28,300	42,800
Taxes and Insurance : (2% of Capital Investment)	14,100	21,400
Depreciation : (10% of Capital Investment)	70,000	107,100
Total Annual Cost:	$324,300	$391,800